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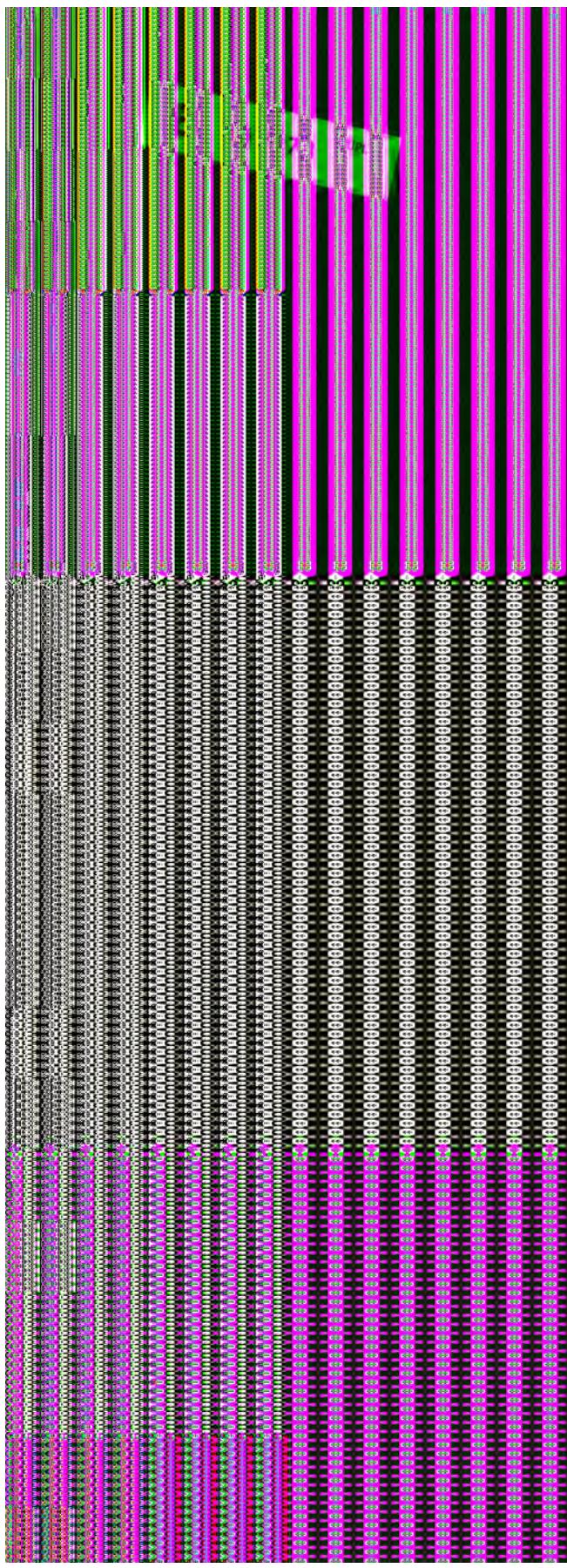
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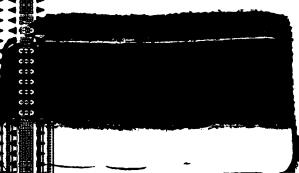
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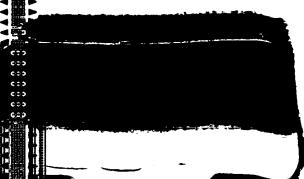
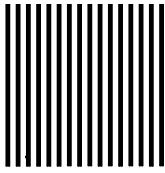
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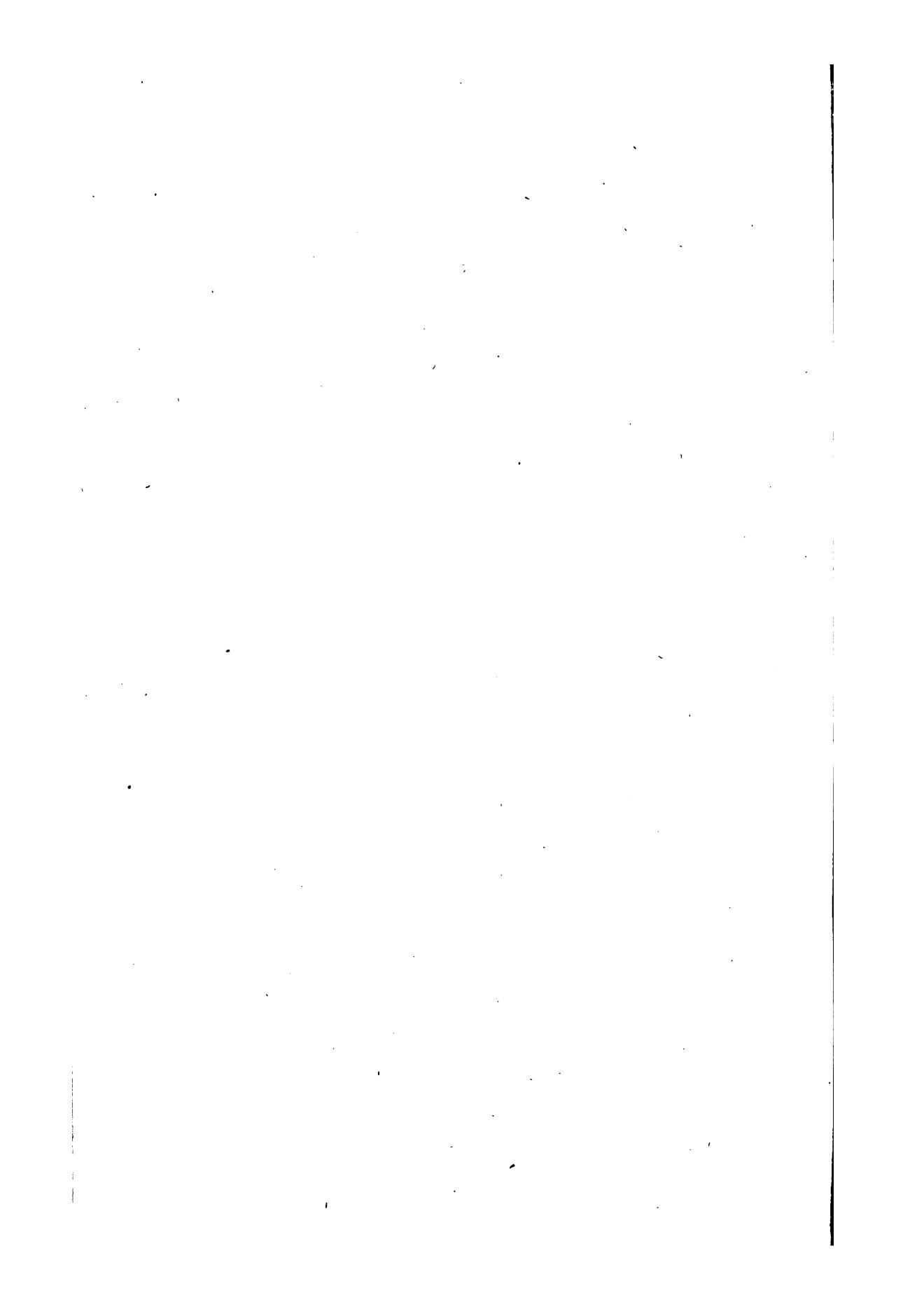
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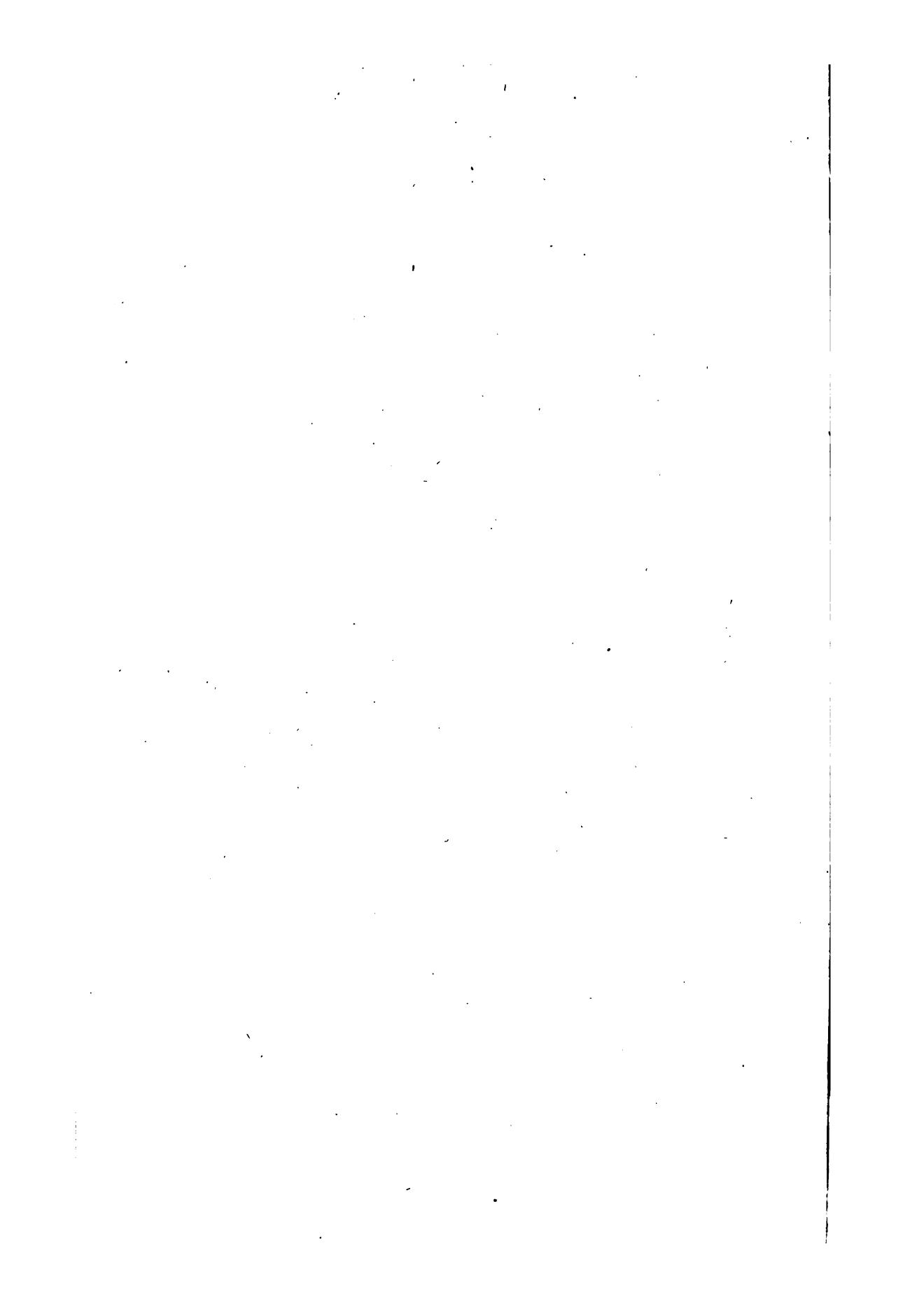
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INTRODUCTORY NOTES  
ON  
QUANTITATIVE  
CHEMICAL ANALYSIS

By  
**CHARLES WILLIAM FOULK**  
*Professor of Analytical Chemistry in the Ohio State University*

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**SECOND EDITION  
REVISED AND ENLARGED**

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1910

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**BY**

**CHARLES WILLIAM FOULK**

## PREFACE.

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The forerunner of this book was a little volume printed in 1898 and containing practically the same selection of laboratory exercises as given in the following pages. This was exhausted in the course of five or six years and was followed by an extended series of mimeographed notes by way of preparation for a second and enlarged edition. These notes contained, in addition to the directions for laboratory work, a great deal of general matter as found in the present pages but not arranged in the same way. They were used several years and were then rewritten in the present form. A limited number was printed and used during a year not only in the author's classes but also by several other teachers. On the basis of this year's experience the whole matter was again gone over and minor changes made. The result is the present volume. It aims to present the beginning work in quantitative analysis in such a way that the student will be led to think more of the general aspects of the subject than of learning merely to carry out a succession of methods.

No claim of originality is made for this idea for it is unquestionably the aim of every good teacher of the subject. The claim is made, however, that in the following pages more than the usual amount of descriptive and explanatory matter is given in its general sense rather than in immediate connection with the laboratory exercises.

The idea that much could be gained by laying greater emphasis on this form of presentation has been growing in the author's mind for a number of years. While the notes previously in use contained fully as much of such general matter as the average text-book, yet it was observed that the majority of the students did not seem able to think of such points apart from their application to the particular laboratory exercise in connection with which they first learned them. For example, the account of how to make a sodium carbonate fusion was given under limestone analysis, and recitations on the subject usually took this trend:

Professor (desirous of developing the idea that all insoluble silicates can be fused). "Describe the method of making a sodium carbonate fusion."

Student. "You take the residue from the limestone—"

Professor (interrupting in order to emphasize the point). "But why bring in limestone? Can not other insoluble material be fused?"

Student (looking blank), "I suppose so."

Professor. "Then describe the procedure of making a fusion so that it will fit any material."

Student. "You mix the residue—"

Professor. "But suppose there is no residue. We have already learned that samples that are not readily attacked by acids are fused directly. Can not a fusion be described in a way to include this condition?"

Student. "I guess so."

So it would go on and after much effort and loss of time, the recitation would develop that fusing with sodium carbonate is a general method for decomposing a certain class of substances, and that there is a proper relation by weight between the material to be fused and the amount of carbonate to employ, and that the fusion is made in a certain way, etc, etc. Similar struggles would be held with other general points, such as ignition of precipitates, filtration, washing, titration and the like, and yet, if by chance the final examination contained the question, "Describe method of making a sodium carbonate fusion," sixty per cent. of the class, at least, would begin, "You take the residue from the limestone—"

There was evidently something wrong with the method of presentation and accordingly the experiment was made of giving as much as possible, even to details of manipulation, in a general way rather than in connection with some specific laboratory exercise. The material of the old notes was rewritten from this point of view, and the results show the value of the new method; for now the large majority of the class, when called upon to recite on the topic of fusing with sodium carbonate, will begin: "The finely ground sample is mixed in a platinum crucible with five or six times its weight of sodium carbonate, etc, etc."

On the other hand, the author does not believe that a study of general procedures will lay a solid foundation for quantitative chemistry unless it is accompanied by a series of thoroughly prac-

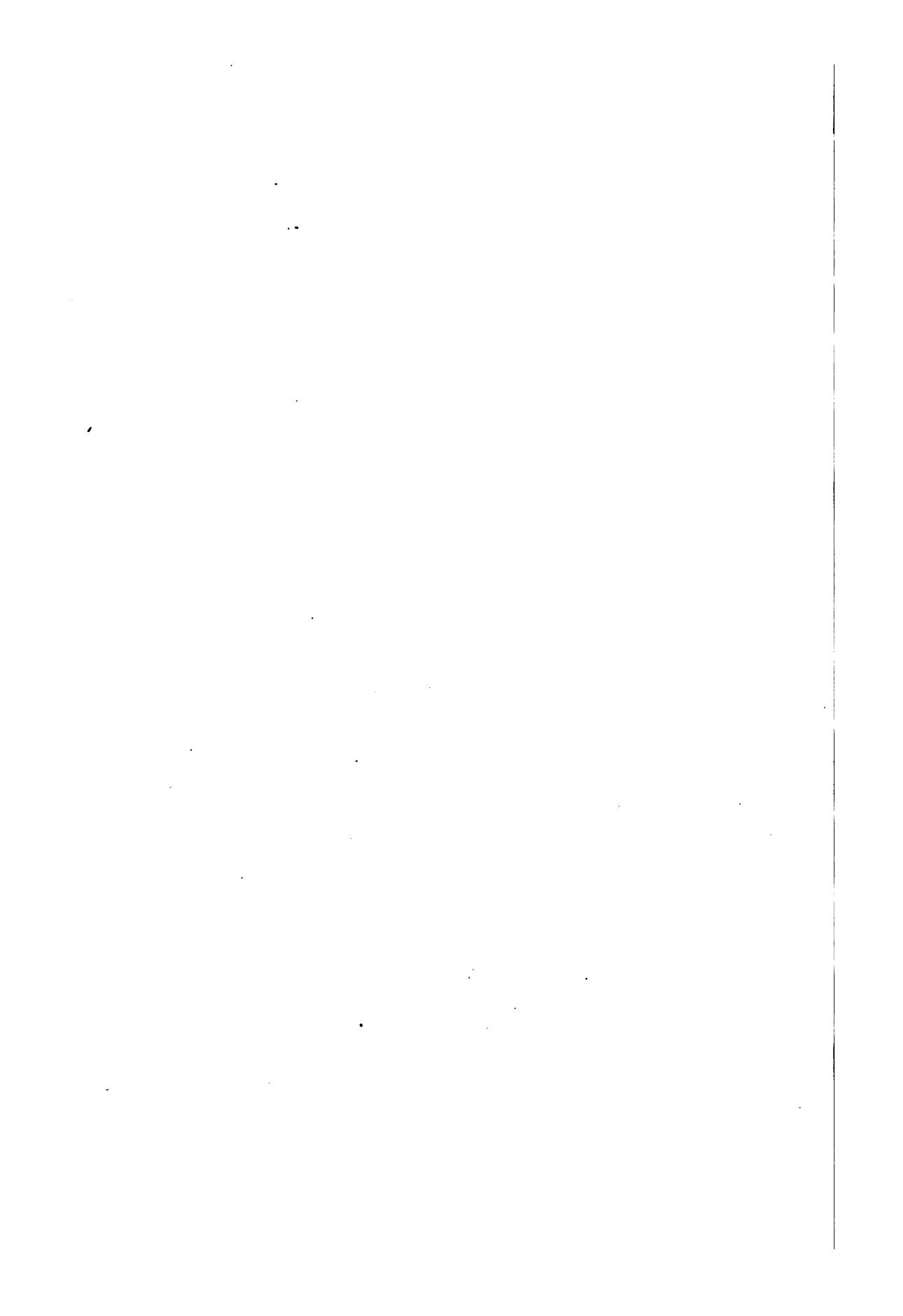
tical laboratory exercises. The nature of this laboratory work is largely a matter of indifference, provided it be graded in point of difficulty, beginning with determinations that are relatively easy, and that it furnish a variety of manipulative experience, and last but by no means least, that constant check be kept on the accuracy of the student's work. It is further a whim of the author that the substances analyzed should in large measure be natural or manufactured commercial products.

In the Ohio State laboratory a line of analyzed samples is kept. These are given to the students by number, the rule being that at least two satisfactory results must be obtained on each determination. In addition, some of the standard solutions are also checked by the instructor. Working in this way and on a basis of four hours a week college credit, the average student occupies a year in accomplishing what is in this book. If more laboratory work is desired, references are given to other textbooks. This is done designedly, for a little practice at the end of the year with laboratory work depending upon references outside the familiar text-book has a value all its own. Small classes can easily use the library and in the case of larger numbers the mimeograph can be brought into requisition to furnish copies of the essential matter from other sources. This has the advantage, not only of giving a certain leeway to the teacher but even of forcing him to take it.

Other points that have received particular attention will only be mentioned. They are: (1) Discussion of errors (sections 34, 35, 78 and 115). (2) The method of treating normal oxidizing and reducing solutions (section 104). (3) The keeping of laboratory notes (sections 73 to 75).

Acknowledgement is made of the help afforded by such works as those of Lord, Talbot, Morse, Treadwell-Hall, Washington, Hillebrand and others. The author also wishes to express here his appreciation of the help and encouragement of his friends and colleagues, Dr. Withrow, Dr. Wilkinson and Mr. Sweeney.

Columbus, Ohio, September, 1910.



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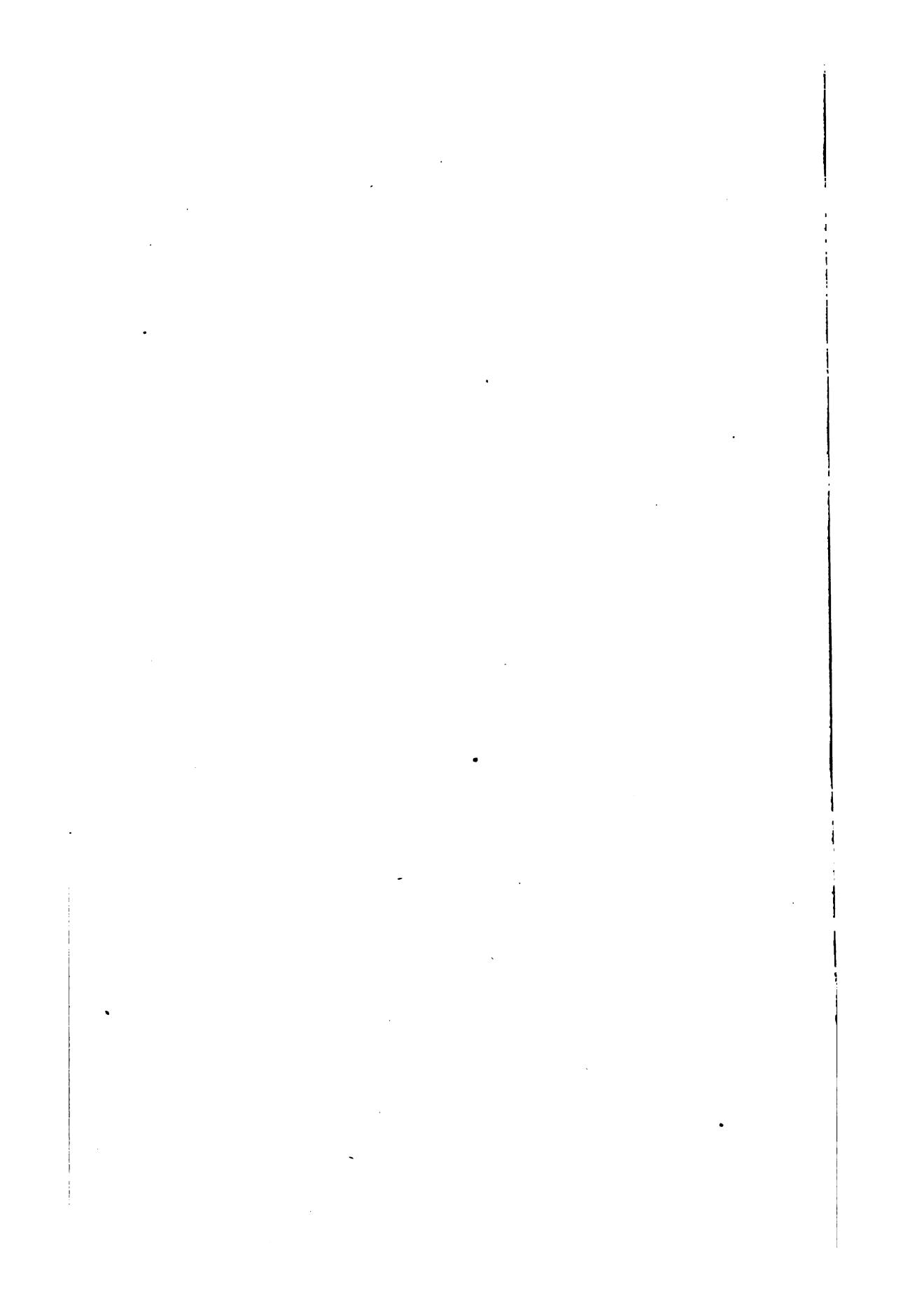
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## PART I.

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### PRINCIPLES OF THE CHEMISTRY AND MANIPULATION OF QUANTITA- TIVE ANALYSIS.

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#### INTRODUCTION.

##### Foreword to Students.

When the element of measurement is introduced into chemical analysis it becomes quantitative and the various divisions of the subject are named according to the constituent to be determined. If this measurement be made with the balance, in other words by weighing, it is called gravimetric analysis. When the amount of the constituent under examination is measured by observing the volume of solution which will react with it, the method is called volumetric. These general divisions of quantitative analysis are the most important and are the ones usually included in an elementary course. Another method of measurement applicable only to very small amounts of substance is called colorimetric and is accomplished by comparing the depths of color produced by the constituent to be measured with that of known amounts of the same substance in the same volume of solution. These three include the great majority of quantitative chemical analytical methods. Obviously each one is limited in its application. Gravimetric analysis can be used only in the case of those substances that can readily be brought to a stable form suitable for weighing. In like manner the other two methods have their special limitations to be learned later.

Many other principles not included under these heads are of course used. Certain optical properties may be measured as is done with the polariscope in sugar analysis. Then again the

content of a solution affects its density and its electrical conductivity and on the measurement of these properties analytical methods are founded. Certain groups of methods are also given names descriptive of the means employed or the character of the material examined. Under such a classification are to be found electrolytic analysis and gas analysis.

In the course in quantitative analysis as outlined in these notes, only the principles of gravimetric and volumetric analysis will be attempted. A graded series of practices beginning with easy methods and gradually working up to those that are more difficult will be given; each practice involving new points in procedure. In the selection of these practices every effort has been made to make them practical. Accordingly, with the exception of the first two, each consists in the analysis of some material, either a natural or artificial product, that comes in the daily routine of commercial laboratories. These substances will be given the student by number. They have been analyzed by the instructor and the student is expected to obtain the same result.

The proper attitude of mind, however, on taking up the subject of quantitative analysis is not to learn methods but the general science of quantitative chemical measurement as applied to chemical analysis. As in other sciences of measurement, accuracy of results within the limits prescribed by the work in hand, expresses in a single phrase the end to be sought. The great accuracy coupled with rapidity of work seen in trained analysts is due largely to the skill which comes by doing the same thing a great many hundred times. For this kind of skill which requires so much time to acquire, the student should wait till he is paid for his time. The beginning university course is the place to learn the fundamental principles of the chemistry of quantitative reactions and of the art of handling chemical substances in a quantitative way, that is, without loss or gain. This art is called quantitative manipulation. The time allotted to such a course permits only a relatively few methods of analysis to be tried in a year. By proper selection of these methods, however, the principles of the chemistry and manipulation of the subject can be illustrated, and it is the general applications of these principles that should be kept in mind. The particular application which can be used in the laboratory work is only one of many hundred. It should be learned and learned thoroughly.

too, but always from the point of view that it is the application of certain general principles.

To emphasize this general point of view as many as possible of the chemical and manipulative details have been brought together and classified in the first part of these notes under the heading, Principles of the Chemistry and Manipulation of Quantitative Chemical Analysis. By the use of numbered paragraphs references to this part are made easy. At first the student need concern himself only with the references in the particular laboratory practice he is on. In a few weeks however the sections on general manipulation should be studied by themselves as separate subjects. For example, in the first week it is necessary to know how to ignite barium sulphate but very soon thereafter the whole subject of ignition of precipitates should be studied as such. A knowledge of these general principles distinguishes the chemist from the man who merely knows how to analyze a few things. The training that comes by keeping this point of view in mind enables one to read new methods understandingly and quickly to acquire skill with them in the laboratory.

As a closing word of advice, read and re-read the descriptive matter. Beginners often keep on day after day doing a thing in an awkward or even in a wrong manner merely because they do not keep themselves familiar with their text-books.

### ***Cleaning Chemical Apparatus.***

**I. Test of Cleanliness.** Glass apparatus is clean when on being rinsed with distilled water and held so the water flows off from it readily, no drops gather. If large drops quickly gather after rinsing it means that the glass is covered with a thin layer of grease. Apparatus in such condition should not be used in analytical work. It must be clean inside and outside. Careless, lazy and sloppy workers content themselves with the phrase, "it's clean on the inside."

**2. Practical Points.** (1). Dust, pieces of straw from the packing, residues of salts, etc., should be washed out with hydrant water. Note—a piece of wide rubber tubing about six inches long attached to the water outlet greatly reduces the splashing.

(2). Ground pumice stone rubbed over the wet surface with the hand and then rinsed off is the readiest way of cleaning the outside of glass vessels. A supply of this material should be kept in a flat dish on the desk.

(3). The inside of flasks and the like is best cleaned with the so-called cleaning fluid. This is made by putting a little chromic acid or some chromate into concentrated commercial sulphuric acid. A good plan is to put 10 to 15 grams of crude potassium or sodium chromate into a half liter, wide mouth, glass stoppered bottle and fill it up with acid. The chromate forms a solid cake in the bottom from which the spent acid can be poured when it is necessary to change it. Mere rinsing with this even in the cold almost instantly removes the surface layer of grease. The sulphuric acid must be concentrated; therefore the bottle must be kept stoppered and vessels to be rinsed with the solution must first be drained of the excess of water. By proper turning and inclining, the fluid can be made to flow over all parts of the inside of a vessel and can then be poured back into the bottle. After a week or so through taking up water it loses in efficiency, when the acid should be poured off from the chromate and the bottle refilled with fresh acid. For cleaning small apparatus such as test tubes, etc., which are covered with organic substances, a large porcelain dish full of the cleaning fluid may be heated and the small articles placed in it.

(4). The crust of calcium carbonate and iron oxide deposited by hard water is best removed by hydrochloric acid. Ammonia water dissolves coatings of silver chloride and of molybdic acid. *No*

(5). Deposits not removable by the above means can often be rubbed off. If it is impossible to get at the place with a test tube cleaner or a swab of cloth on the end of a stick or a glass rod, it can be accomplished by shaking a handful of small shot and a little ground pumice in the vessel. This is more efficient if just moist rather than when used with an excess of water. For rubbing the inside of long tubes of small bore a string with a knot in the middle which can be pulled back and forth is the simplest scheme. The string can be put through very small tubes by means of a stream of water.

(6). Finally, whatever method of cleaning is used the apparatus should be rinsed with distilled water. The best way is to use several small portions causing it to flow over the entire surface.

As a rule only the outside of beakers is wiped dry. It is best not to touch the inside with anything of such doubtful purity as the laboratory towel.

(7). Attention must also be given to apparatus of the character of ring stands and filter stands. If they are rusty and covered with dust some of it is sure to get into the solutions. All such apparatus should be wiped or brushed off each time before use. Neat workers are also recognized by their keeping the tops of their desks sponged off and the lockers and drawers clean and in order.

### **Simple Glass Working.**

The student of analytical chemistry should learn as soon as possible the simpler methods of glass working.

3. **Kinds of Glass.** Three kinds of glass are in common use about the laboratory. Hard or potash glass is used for combustion tubes and for other purposes requiring a high temperature. This glass can be recognized by the green color, blue-green in the case of Jena glass, best seen when looking at the end of the tube. It softens only in the blast lamp flame and is therefore very difficult to work. Beyond cutting, bending and drawing to a point, working with it should not be attempted by the beginner. The same can be said of lead glass which is a very soft special sort used chiefly when platinum wires are to be sealed in. Soft or soda glass is the sort from which practically all of the common forms of apparatus are made. It can be recognized by the black appearance seen on looking at the ends of the tubing.

4. **Cutting Glass.** For small or medium sized tubing a short file scratch is made at the desired point and a bending stress applied. As a rule the tube breaks square across. When the tube is to be cut off so near one end that there is no room for holding on that side, a file scratch is made as before and one end of this scratch touched with a bead of red hot glass. If this does not result in producing a crack another trial should be made, eventually trying the other end of the scratch. This method is also used for cutting off large tubes. The crack, however, in the case of a large tube will not as a rule extend clear around. Here advantage can be taken of the fact that a crack in glass can be led in any desired direction, even turned at right angles, by drawing just in front of

it a piece of red hot iron like the end of a file. A good workman will always make a line around the tube with a glass pencil or by tying a string around it to serve as a guide. A special instrument for cutting large tubing is on the market and is of great advantage when at hand.

**5. Bending Glass.** The fish-tail burner with the yellow flame, or even better, an ordinary illuminating tip is best for amateur bending excepting in the case of large tubing. Beginners should not attempt to bend small tubing in the Bunsen or blast flame. Two points of importance are to be noted. First, on the length of glass heated will depend the character of the bend. If only an inch or so of the glass is softened the bend will be short and abrupt. For a bend involving a longer curve, or when the glass is to be bent through a considerable angle, the flame is turned up and two or three inches of the glass heated. Second, to keep the bent portion in the same plane the tubing should be held while bending on a piece of asbestos or unpainted wood. Other points of value are to mark out the work in advance on the board or asbestos and bend to the marks. This is especially valuable when making a number of pieces of the same sort, or when a rather complicated piece of bending is to be done. When several bends are to be made in the same tube, it should always be noted beforehand just how the glass is to be held when making the bend.

Sometimes especially with thin walled tubing the bent portion will be flat. This can be remedied by closing one end of the tube by drawing it out (6) and then using a small blast flame, heating the flat place in small areas at a time and blowing them out with the mouth. This method is not very difficult and requires much less experience than to heat the flat portion all at once and blow it out.

Large tubing can be bent by heating short lengths in the blast flame and bending each portion through a small angle. This makes a very wide bend, but it is the only way in which a beginner can hope for success. Each bend should be made on a piece of asbestos to keep it all in one plane.

**6. Drawing Out a Tapering Point.** To do this free-hand the following procedure should be employed: The end of the tube to be drawn out is first heated in the blast flame and touched with a piece of scrap glass which at once adheres and permits of drawing out a thin point several inches in length which will serve as a handle

so to speak, for manipulating the glass in making the finished taper. The scrap glass is broken off at once, and, grasping the drawn out end, the tube is rotated in the flame and by letting the walls thicken and at the same time making a series of short pulls, the end can be drawn down symmetrical and with the walls the same thickness as the rest of the tube. The point to observe is constant rotation, and if it is seen to draw more to one side than the other, a little harder pull should be made away from that side to get it straight. A simple trick which avoids many of the difficulties is to turn the blast flame horizontal and then holding the tube vertical rotate it in the flame. The weight of the glass below the flame exerts a steady pull which can be regulated to a nicety by allowing more or less of the glass in that position. Sometimes a piece of scrap glass can be put onto the lower end with advantage.

**7. Sealing Glass Tubing Together.** The end of one of the pieces to be joined should be closed to permit the subsequent blowing. The ends to be joined—they should be cut square across—are brought to a soft heat and are then put together, care being taken to make them coincide at first as they adhere the moment they touch. (If the elbows be held against the sides the hands will be found steadier. This point is to be remembered when rotating soft glass in the flame.) The ends having been brought together the joint is rotated for several moments in the flame to heat it uniformly, and by appropriate manipulation to bring the tubes straight. The blast flame is now turned to a point and the joint blown out by heating and blowing one small place at a time. When this process is finished there will of course be a small ring blown out which must be brought to the diameter of the tubes by heating and pulling. The tubes can be brought into line by gentle pulling while rotating. When the tubes to be joined are of different diameters the larger one is drawn down.

**8. General Points in Glass Working.** Glass heated to the point of softening tends to flow together. The walls of a tube can easily be thickened by rotating it in the flame without pulling. The drawing out of the ends should always be done when beginning any operation. It closes the end for subsequent blowing and saves glass by making a long handle out of only the fraction of an inch of the tubing. Being so thin, the drawn out piece cools almost at once.

The regulation of the blast lamp flame for the different operations of glass blowing is of the greatest importance but very difficult to describe without accompanying demonstrations. The student should experiment while working, using a larger or smaller flame till it appears that the proper size has been found. Generally speaking, a small flame is used since it is desirable to heat the smallest possible quantity of glass to a soft heat at one time. This will prevent distortion of the piece while working.

When a piece of work has once been started it must as a rule be finished before allowing the glass to cool. Otherwise it will crack.

At the end of any operation in glass blowing the part should be brought almost to a soft heat by rotating in the flame. The piece is then set aside in such a way that the hot part does not touch anything. This uniform heating and subsequent slow cooling anneals the glass sufficiently to prevent cracking when it becomes cool. Sometimes after the final heating in the blast flame the piece is held in the yellow flame till it is thoroughly coated with soot. Under these conditions the cooling takes place more slowly and the annealing in consequence is better.

Different kinds of glass cannot be fused together, at least not by beginners.

Many of the methods described above are not those used by professionals, but though not so good in themselves they are better adapted to amateur workers.

#### **The Outfit for Quantitative Analysis.**

Before constructing the special apparatus described below, the sections on glass working (3 to 8) should be read.

In addition to such pieces as beakers, dishes, burners and the like which are ready for use, a number of things must be fixed by the student.

**9. Wash Bottles.** Two will be needed, one of 1000 cc. capacity for cold water and one of 500 cc. for hot water. In the construction of a wash bottle the following points are to be observed: (a) The two-holed stopper should be of rubber and fit the flask so

that it sits firmly in place when about half way into the neck. If further than this it is difficult to remove, and if less there is danger of its popping out when using the bottle. (b) The mouth-piece A (Fig. 1) should go just through the stopper thus permitting all of the water to be poured out. It should be bent at an angle of 45 degrees, the middle of the bend coming about one inch above the stopper. Seven to eight inches is a convenient length. (c) The water tube B should reach the bottom of the flask so that all of the water can be blown out. An extra refinement is to bend it at about the neck of the flask so that when the bottle is held in the customary position for use the end of the tube is at the lowest point as shown by the dotted line in the figure. This is done by bending it in the same plane and towards the same side as the upper end. The upper end should be bent through an angle of 135 degrees, the bend coming about an inch above a line drawn through the mouth-piece. (d) The nozzle C should be about two inches long and be drawn out so the walls of the tapering portion are of the same thickness as those of the tube. It is connected to the water tube by a piece of soft gum tubing, a space being left between the two pieces of glass just long enough to permit of its being pinched between the fingers. The water tube should be cut off at such a length that when the bottle is in use the fore finger just reaches that part of the nozzle covered by the soft rubber. (e) The neck of the hot water bottle should be wrapped with cloth to protect the hand.

10. **Desiccators.** A desiccator is a specially designed vessel in which a dry atmosphere is maintained by substances that readily absorb water. It is usually fitted with a ground glass cover and so designed that the drying material is placed in the bottom, a support for the object to be placed in it being just above. A triangle is commonly employed as the support since crucibles are the usual

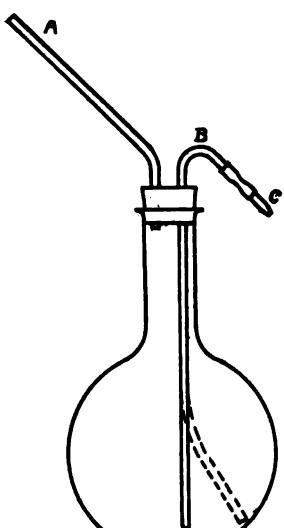


Fig. 1.

objects placed within. This triangle should be fitted carefully by cutting or bending the wire ends so that when in place it sits firmly. The desiccator can then be carried about with but little danger of upsetting the crucible. Nickel wire makes a neater support than the clay triangles. By exercising a little ingenuity two triangles can be combined so as to furnish supports for two crucibles. The desiccating substances that may be used are phosphorus pentoxide, concentrated sulphuric acid and calcium chloride. Of these the pentoxide is the most efficient, the others following in the order named. Only the sulphuric acid and calcium chloride are commonly used in quantitative analysis. Sulphuric acid is perhaps the better but does not permit of the desiccator being carried about owing to danger of splashing the acid. This can be remedied by filling the lower part with glass beads or even with broken glass. Calcium chloride, however, being a solid is generally used when the desiccator must be carried to and from the balance room. A trace of vaseline should be put onto the ground glass parts to insure an air-tight joint.

11. **Stirring Rods.** Six should be made by cutting glass rod into the proper lengths and rounding the ends in the blast lamp flame. Four, eight inches long and two, five inches long are convenient. The rod should be about  $\frac{3}{16}$  inch in diameter.

12. **"Policeman."** This is a piece of heavier rod about  $\frac{1}{4}$  inch in diameter and eight or nine inches long, over the end of which a piece of soft gum tubing about an inch long is drawn. The tubing is cut off on a long bevel and allowed to project a little beyond the end of the rod. The instrument is used for rubbing the inside surface of beakers to remove adhering precipitates.

13. **Filling and Labeling Reagent Bottles.** Prepare 500 cc. bottles for hydrochloric and nitric acids and for ammonia. A 250 cc. bottle will serve for sulphuric acid. These bottles are to be labeled by pasting onto them gummed labels lettered with the appropriate formula. A soft lead pencil or India ink is the best medium for doing the lettering. If, after the paper is dry, a thin layer of paraffine or shellac be applied the label will last much longer. Other bottles should be labeled and filled as needed.

Owing to the irritating fumes from strong solutions of hydrochloric acid and ammonia, these reagents should be diluted. A good plan, after cleaning and labeling the bottles, is to fill the one for hydrochloric acid half full of distilled water and the one for

ammonia two-thirds full. They can then be taken to the store room to be filled up with the strong acid and ammonia solutions. For an occasional experiment demanding the use of concentrated acid a small amount can be obtained in a special bottle.

14. **Silver Nitrate Bottle for Chlorine Test.** (Fig. 2.) All washings must be tested and in the great majority of cases the test is made for chlorides. This requires that silver nitrate be added in the presence of nitric acid. If the silver nitrate solution (approximately 5%  $\text{AgNO}_3$ ) be diluted with an equal volume of concentrated nitric acid, no additional acid need be added when water is used for washing. In the exceptional case when an alkaline solution is used more nitric acid may be needed.

For convenience this silver nitrate acid mixture should be kept in a small bottle (about 100 cc.). A cork just too large for the bottle should be cut in two and bored to carry a glass tube about  $\frac{5}{16}$  inch in diameter. This tube should be drawn out slightly at one end and the other end rounded. It should reach nearly to the bottom of the bottle and project about three inches above the neck. Fitted in this way with the cork merely resting on the top, the tube carrying the necessary amount of solution for a test can be lifted out with one hand.

15. **Platinum Wire.** This is used chiefly for stirring precipitates in the crucible to hasten combustion. For this purpose it is best to bend it into the form of a loop and grasp the ends where they cross with the crucible tongs. This is better than when fused into a piece of glass.

#### **The Balance.**

For a general description of the theory and construction of balances the student should refer to any large text of analytical chemistry or of physics. In the chemical dictionaries will also be found articles on this subject. Certain points on the use and care of the analytical balance must, however, be learned before beginning work.

16. **Construction.** Sitting in front of the balance the student should study the details of its construction, noting carefully the function of each part and the mechanism by which the arrest,

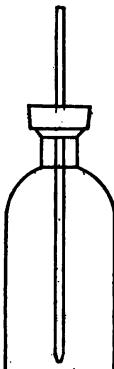


Fig. 2.

the various adjustments, the manipulation of the rider, etc., are accomplished. With an illustrated description before him or after seeing the instructor take a balance down, the student need not hesitate to take off the pans and stirrups by which they are suspended and even remove the beam. When in one's own laboratory this must sometimes be done in order to clean the instrument. It must, however, not be forgotten that a balance is a delicate and expensive piece of apparatus and must be handled accordingly. The pans, stirrups, etc., are marked to indicate the side, right or left, to which they belong.

17. **The Rider.** The scale on the beam is usually marked so that the zero point is over the middle knife edge and the divisions are numbered from this towards both ends. In some makes of balances the zero is on the extreme left of the beam the marks being numbered past the middle to the right end. With this construction the rider must be on the zero mark when the equilibrium of the empty balance is tested. The proper weight of the rider can be told by an inspection of the number of divisions into which the beam or one of its arms, as the case may be, is divided. The rider should weigh in milligrams the number of whole divisions from the middle knife edge to the end knife edge, or in the event of the zero point being at the left end of the beam, the number of divisions between the end knife edges. It should be noted carefully that the above reads, "the number of divisions from the middle *knife edge* to the end *knife edge*," etc. The actual figures on the beam may not extend as far as the end knife edge. In this case, however, it can easily be seen what the number would be were the actual scale so extended. Sometimes the scale extends beyond the knife edge at the end, but in all cases it is the number of divisions between the knife edges that determines the weight of the rider. If the weight of the rider did not correspond to the divisions of the beam, weighings could still be made with it but an extra calculation would be necessitated in each case. When its weight does so correspond, its position on the scale at once gives the figures for the third and fourth places of the weight of the object being weighed.

18. **Permanent Adjustments.** When the beam is raised the various knife edges and planes should be just out of contact with each other. This can be seen by having a bright light on the other side of the balance from the observer. If a knife edge and its plane

are too far apart they quickly become worn from the shock of contact when the beam is lowered, and if in contact all of the time they deteriorate from the constant pressure. The three knife edges must be parallel and at right angles to the beam. Were this not the case the distribution of the load would change during the oscillations of the beam. The three knife edges must also lie in the same plane. If the middle one were above the other two the sensibility of the balance would be diminished largely with an increasing load because the center of gravity would be lowered. If the middle knife edge were below the end ones the sensibility of the balance would increase with increasing load but the center of gravity might be raised above the axis of rotation of the beam which would result in unstable equilibrium and it could no longer swing. For convenience sake the two arms of the beam should be practically equal in length. The above adjustments are all made in the factory and should never be attempted by an inexperienced person.

Certain other adjustments, however, must be made from time to time and these the student should learn at once.

**19. Location and Leveling.** A balance designed for fine weighing must be set on a solid support where it will be protected from vibrations. The case must be leveled and for this purpose screw adjustments are provided on the bottom and on the inside is a spirit level or plumb bob. A balance must also be protected from unequal heating. The sun shining on one end of the beam renders the instrument worthless till the temperature difference is equalized. An alkaline substance like quick lime or sodium carbonate is sometimes kept in shallow dishes in the balance case to neutralize acid vapors and take up the excess of moisture.

**20. Zero Point.** When in perfect adjustment the zero point of the balance corresponds to the zero of the pointer scale. This means that if the beam with no load in the pans be caused to vibrate, the pointer will move an equal number of divisions on each side of the pointer scale and if allowed to come to rest will do so at the center of this scale. Practically this condition need not be fulfilled as it would necessitate too frequent adjustment. It is sufficient if the zero point of the balance is within one division of the middle of the pointer scale. If on trial it be found off more than this the little nut on the end of the beam should be screwed in or out till the pointer swings more nearly the same on both sides. The exact lo-

cation of the zero point is not determined by making the experiment to see where the pointer will come to rest but by calculating the location from data obtained by noting the places on the scale at which the pointer turns back when swinging.

(1). A proper procedure is to make three observations on one side and two on the other. Tenths of a division can be estimated. The average is found for each side and then the average of these two. The final result so obtained is one half of the average distance covered by the pointer from turning point to turning point. This is subtracted from the greater average distance on one side of the middle point of the scale. The result is the place at which the pointer would come to rest. For example:

Left.	Right.
8.5	7.2
8.2	6.8
<u>7.9</u>	<u>2) 14.0</u>
3) 24.6	7.0
8.2	
<u><math>\frac{8.2+7.0}{2}=7.6</math></u>	$8.2-7.6=0.6$

The zero point of the empty balance is 0.6 division to the left of the middle of the pointer scale. This method of determining the zero point involves considerable time in making the observations and in a certain sense introduces a chance for blundering because of the calculations required. For the practical requirements of general analytical work the following method is to be preferred.

(2). After a preliminary trial to see if the pointer swings within two divisions at least of the same distance on each side of the scale, the second and third half swings are observed and the difference between the two noted. For example, suppose the pointer turns at 7.5 on the right, 6.3 on the left and 7.2 again on the right. The difference,  $7.2-6.3=0.9$ , is to be noted and when concluding the weighing of an object, equilibrium is considered established when the pointer swings the same way, that is, 0.9 division more on the right than on the left. This difference in swings is to be found each time a weighing is made when the balance in question is one used by several students.

**21. Sensibility.** The sensibility of a balance is its response to a small excess load on one side. It can be expressed most conveniently in terms of the divisions on the pointer scale by defining it as the difference between the zero point of the empty balance and the same with a load of one milligram on one side. When using the more rapid substitute method above for the zero point (20, 2) the sensibility can be defined as the number of divisions more on one side than the other that the pointer swings with an excess load of one milligram on one side. The sensibility can be regulated by a small nut or sliding weight that can be raised or lowered. This is to be found on the pointer or above the middle knife edge. Raising this raises the center of gravity of the beam and increases the sensibility while lowering it has the opposite effect. In changing this adjustment it must not be forgotten that the equilibrium will also be disturbed and must be adjusted. It will be observed that the more sensitive a balance is, the slower will be the vibration of the beam, consequently weighing is very tedious with an over adjusted balance. For ordinary analytical work one milligram should cause a deflection of about five divisions. With a good balance the sensibility should change very little with the load. In any event it can easily be determined at several points, for instance with no load in the pans, with five grams in each pan, with twenty grams, etc.

**22. Pan Adjustment.** An arrangement is provided for supporting the weight of the pans when the balance is not in use. It should be adjusted so that the pans are just prevented from swinging when the beam is arrested. The mechanism differs among the different makes of balances but is usually so simple as to be apparent at once.

**23. Cleaning the Balance.** Dust can easily be removed from the beam by brushing with a soft brush. After long use it becomes necessary to clean the knife edges and planes. This is best accomplished by wiping them with a soft cloth moistened with alcohol. Great care should be used to avoid touching the metal parts with the alcohol as it would destroy the lacquer. Anything in the nature of a thorough overhauling of a balance should of course be left to an expert in such matters.

### The Art of Weighing.

A regular procedure should always be followed when making a weighing. Time is saved and what is of still greater importance the chances of committing a blunder are reduced by having formed the habit of working always by a certain well thought out plan. The scheme below can be carried out rapidly and is sufficiently accurate for ordinary work. After a week or two when the use of the balance is somewhat familiar, the sections on special methods of weighing and the general one (26) on degree of accuracy should be studied.

**24. Procedure in Weighing.** (1). Dust off the pans with a soft camel's hair brush. One with very long bristles is best.

(2). Try the swing of the pointer (20, 2). A trick of lowering the beam in such a way as to cause the pointer to swing can quickly be acquired. Another method is to drop or raise the rider for a moment. In any event the balance case must be closed when the final observations are made. Erratic behavior of the balance is likely to be due to, (a) the beam touching the rider or its carrying mechanism; (b) a pan touching some object in the balance case; (c) a displaced stirrup; (d) a fly on the beam.

(3). Place the object to be weighed on the left pan. Crucibles, watch glasses, large pieces of metal, etc., can be put directly onto the pan. Chemicals of all sorts and powdered material in general must be weighed on a watch glass or in some suitable vessel. Both the object being weighed and the heavier weights on the other pan should be in the center so the pans will hang straight.

(4). Find the weights necessary to counterpoise the object. An exact system should be followed. The only guess permissible is in the selection of the first weight. This should be chosen so that, taken with those below it, the weight of the object will be reached. To avoid the possibility of having to remove a large number of small weights and begin the second time, the first piece tried should be on the side of too heavy rather than too light. The method can be illustrated best by an example. Suppose the object to be weighed is a platinum crucible which the chemist estimates weighs from 30 to 40 g. The weights in the box have the following values: brass weights, 50, 20, 10, 10, 5, 2, 1, 1, 1; small weights, 0.5, 0.2, 0.1, 0.1, 0.05, 0.02, 0.01, 0.01. To avoid the chance of starting wrong the 50

gram weight is first placed in the middle of the right hand pan and the beam gently lowered. The pointer at once shows 50 g. to be too heavy. The beam is raised, the weight removed and the 20 g. piece tried in the same way. This being found too light one of the 10 g. pieces is added. It is still too light. The other 10 g. piece is also put on and found to be too heavy. It is removed and the 5 g. piece is added. This is also too heavy and is replaced by the 2 g. piece which proves too light. Two 1 g. pieces are now added one after the other but they are found insufficient. At this point there would be no use in adding the third 1 g. piece for this would make a total addition of five grams to the thirty which were on when the five gram piece was tried and found too heavy. One begins therefore with the small weights trying them one after the other till the right ones have been found. To facilitate subsequent reading the small weights should always be placed in order on the pan making two rows corresponding to the two decimal places represented. For instance, if the 0.5, 0.2, 0.1, 0.02, 0.01 and 0.01 g. pieces were used they should be laid on the pan so that the 0.5, 0.2 and 0.1 form one row and the 0.02 and two 0.01's the other. Finally the balance case is closed and the rider placed on the beam so that the swing of the pointer will be the same as that with no load on the pans.

(5). Observe the following general rules: Never place an object on the pan or remove it without first arresting the beam; never arrest the beam excepting when it is horizontal or nearly so; never lower the beam suddenly.

(6). Read and record the weights. One of the commonest sources of error among beginners is incorrect reading of weights, therefore a system of checking must be learned at the start and rigidly followed. Suppose the crucible (4) above weighed 34.2346 g. The brass weights used were the 20, 10, 2, 1 and 1. The small weights were the 0.2, 0.02 and 0.01. These pieces being on the pan their places in the box would of course be empty. Now it requires but a few days experience to recognize the holes in the box as readily as the weights themselves. This furnishes the basis for an independent check on the reading. The holes are first read, adding the values mentally and the result set down in the note book. Then without removing them from the pan, the weights themselves are read and the result checked. Finally the reading and checking are repeated a third time when returning the weights to

the box. The position of the rider is also to be checked at each reading of the weights.

(7). The above details of handling and reading the weights may seem at first to be cumbersome and even "cranky." The necessities of the case, however, demand a systematic way of working. In finding the proper weights to counterpoise an object, a hit-and-miss style of selecting them would be found on an average to take more time than the systematic one described above. Still more important is the matter of double checking when reading and recording the weights, for inexperienced students do not appreciate how easy it is to make a mistake at this point. The above directions should be followed to the letter.

**25. Relative Weights.** In quantitative analysis where the results are given as percentages the absolute weight of an object is not needed. The relative weight of the constituent sought as compared with the portion of the original substance taken, the sample, serves every purpose. For example if 1.0 g. of material be examined and be found to contain 0.1 g. silica, the percentage of silica is 10. Suppose now weights were employed so incorrect that the "one gram" piece weighed only 0.9 g. but the rest of the pieces were in proportion, that is, the 0.1 g. weighed 0.09 g. and so on. 0.9 g. (called 1.0 g.) would be weighed and be found to contain 0.09 g. (called 0.1 g.) silica. The percentage of silica is again 10. As long as the relative values are found, the absolute values add nothing to the accuracy of the percentage result. If however one were selling gold by the gram, the purchaser would hardly be content with weights ten per cent. short, however well they might agree among themselves. Gross inequality in the arms of the balance beam would also not affect a final percentage result provided both sample and resulting precipitate were weighed in the same pan. Many other errors are also eliminated by the fact that as a rule the weight actually sought is the difference between two other weights as, for example, the weight of a crucible and precipitate minus the weight of the crucible. The true weight of the crucible is not obtained owing to the different buoyant effect on it of the air (26, 4) as compared with the brass weights. However, since this error is the same in both cases it is eliminated and the only error is the different buoyant effect of the air on the precipitate as compared with the weights. The precipitate is likely to be about the same specific

gravity as the original sample so this error in turn becomes negligible. Occasionally on the other hand the absolute weight of an object is wanted as in certain situations that may arise in calibration of volumetric ware, and the student will do well to think now and then as to what is actually needed in a given experiment and modify the procedure accordingly.

**26. Degree of Accuracy.** Weights are usually given through the fourth decimal place and the first inference perhaps on the part of a beginner is that they are accurately defined to this extent. A good balance indicates differences in weight of 0.0001 g. but this very sensibility to inequalities of load also responds to very slight changes in other conditions such as temperature and mechanical disturbances. A tenth of a milligram more or less in the apparent weight of an object may also be due to its being a little cleaner at one time than another, to a slight difference in temperature, more or less moisture in the air, a slight electrical charge or various other causes. The skill and care with which the weighing is made is another factor which may easily affect the fourth place, and finally if the absolute weight is wanted a correction for the buoyant effect of the air must be made (4). All this presupposes too, that the weights are correct within these limits; an assumption not at all safe after some weeks in a sophomore balance room. Fortunately for most purposes in quantitative analysis the weights of objects do not need to be defined through the fourth decimal place (35) and the disturbing conditions referred to above have as a rule small effect. The result is, that under favorable conditions even in a balance room used by a large class of beginners the relative weighings have no greater error than three or four tenths of a milligram.

In special cases however it may happen that the disturbing influences are greatly exaggerated and it is therefore desirable that they be studied in some little detail as follows:

(1). The weights must be correct, that is, agree among themselves and if the absolute weight of an object is wanted the absolute standard of the weights must be obtained. The standardization of a set of analytical weights is such a time consuming process and requires such favorable conditions in the use of the balance that it is not given in this course. (See Richards, Jour. Am. Chem. Society Vol. 22, 144).

Even beginning students, however, should test the weights occasionally by comparing two pieces or groups of the same weight, as the two 10 g. pieces or the 20 g. with the two 10 g. pieces. When this is done the method of weighing by substitution (27) should be used.

(2). The object weighed must be at the temperature of the balance. Even a slight difference affects the apparent weight by making it lighter if warmer and heavier if cooler. This point must be kept in mind constantly since so many objects are prepared for weighing by previous heating. For very careful work crucibles and the like must be left in the desiccator for forty-five minutes to an hour or until one can be sure that the temperature of the balance room has been reached. In the case of ordinary work, however, it is permissible to make trial by lifting the crucible from the desiccator with the tongs and touching it lightly to the back of the hand. It should feel cool before it is ready to weigh.

(3). The collection of a film of moisture on objects is also a disturbing element. This does not mean of course visible drops but an invisible condensation differing in amount according to the humidity of the atmosphere. In analytical work this is usually compensated (25). Occasionally, however, even for relative weights, when large objects are weighed, as the potash bulbs and guard tube of the carbon dioxide determination, the effect is so great and so variable in warm weather that the method of weighing by tares (28) will save time.

(4). The buoyant effect of the air must be considered when the absolute weight is wanted. Very few of the objects usually weighed have the same specific gravity, that is, the same volume weight for weight as the metal of the weights. Glass and porcelain especially are much bulkier with the result that they displace more air than the weights and therefore seem lighter than their true weight. Since a cubic centimeter of air weighs on an average 0.0012 g. the error introduced, it is seen, is considerable, if there is even a fraction of a cubic centimeter difference in volume between the object and the weights. In the case of a porcelain crucible weighing about 16 grams the error amounts to over 0.0050 g., an amount quite beyond the degree of accuracy required of even a beginning student.

In the relative weighings of most quantitative analyses the error is eliminated by the nature of the method (25) but it occasion-

ally happens that the absolute and not the relative weight is wanted and it is therefore necessary to understand the situation. In calibration, for example, when the volume of a given mass of water is calculated from its weight a very considerable error would be made by disregarding this correction. Under calibration the correction is included in the table given there, and it suffices here to call attention to this application and to give the general formula for calculating the true weight.

$$W = P + P \times 0.0012 \left( \frac{I}{D_1} - \frac{I}{D_2} \right)$$

$W$  = vacuum weight required.  $P$  = apparent weight found by weighing the object with brass weights in air.  $D_1$  = specific gravity of the object and  $D_2$  the specific gravity of the weights.  $0.0012$  = weight of a cubic centimeter of air. The specific gravity of the brass of the weights can be taken as 8.4. For making a preliminary calculation to see if the error introduced is larger than allowable for the work in hand (35) only the brass weights need be considered. A refined application of this correction is beyond the scope of these notes.

**27. Weighing by Substitution.** The difference in the lengths of the arms of the beam is sometimes sufficient to affect the apparent weight of an object according to the pan it occupies. When an absolute and not a relative weight is wanted this must be taken into consideration. It must be used for example when weights are tested. The method consists in placing the object to be weighed on one pan and counterpoising it by placing any stable material on the other. This counterpoising is accomplished most conveniently by using the weights from another box. When equilibrium has been established the object being weighed is removed and weights put in its place till equilibrium is again obtained. Obviously the object in question and the weights substituted for it have the same weight (26, 4). If two pieces or groups from a box of weights are to be compared, one is counterpoised with weights from another box and then removed and the other put in its place. If both have the same weight, the equilibrium will not be disturbed. If there is a difference it can easily be detected and determined (29).

**28. Weighing by Tares.** The principle of this method is to have an object on the other pan of the same material, size and

shape as the one being weighed. For example, in weighing the potash bulb and guard tube used in the determination of carbon dioxide, another bulb and tube of the same size and filled in the same way are placed on the right pan. The theory is, that both being of the same material and extent of surface, are affected alike by moisture and other disturbing influences. The error due to displacement of air is also eliminated since each displaces the same amount.

This arrangement naturally complicates the weighing, making it rather confusing at first. The scheme will be understood better and the chances of blundering in its use reduced if the tare object be made slightly lighter than the one to be weighed. The tare can then be looked upon as an extra piece in the set of weights. Additional weights will be required only on the right pan, their accustomed place, thus preventing confusion by a departure from the regular method of handling them.

An example of a weighing by this plan is as follows: (See Determination of Carbon Dioxide.)

$$\begin{aligned} \text{Bulb and Guard} + \text{CO}_2 &= \text{Tare} + 0.5148 \\ \text{Potash Bulb and Guard} &= \text{Tare} + 0.1264 \\ \text{CO}_2 &= \overline{0.3884} \end{aligned}$$

This method of weighing must also be used when precipitates are weighed on dried filters. (63).

**29. More Exact Methods of Weighing.** For the regular routine of analytical work the method of weighing as described in 24 serves every purpose and in the first year of his work the student of quantitative analysis has no occasion for the more exact methods. Nevertheless as a matter of interest a brief description of a more accurate procedure is given. When the student reaches the point where the nature of his work demands such exactness he will be qualified to understand and apply these modifications and will have access to a balance so located as to protect it from outside influences that ordinarily render useless such refinement of manipulation.

The more exact procedure is as follows: The zero point of the empty balance is first determined by the method of swings (20, 1). The object is then counterpoised by weights in the usual way (24, 4) excepting that the rider is placed on that milligram mark

which comes nearest to producing equilibrium. The zero point is again determined by the method of swings and the rider then moved forward or backward, as the case may be, one milligram and the zero point determined as before. The difference between these last two zero points with a difference in load of one milligram is the sensibility of the balance under the conditions of load, etc., that exist at the conclusion of the weighing. From it the load that must be added (or subtracted) to make the zero point correspond with that of the empty balance can be calculated. For example, the zero point of the balance is found to be 1.2 on the left of the pointer scale. With an object and weights of 17.436 g., the zero point is 2 on the right. The load is now increased to 17.437 g. and the zero point found to be 3.7 on the left. The sensibility with a load of 17.0 grams is obviously 5.7 divisions per milligram. The difference between the zero point with no load and that with 17.436 g. is

3.2. The correct weight of the object is therefore  $17.436\text{ g.} + \frac{3.2}{5.7}$  milligram = 17.43656 g.

The above procedure it is true can be shortened somewhat but always at the expense of a slight decrease in accuracy. The method can be used with any of the special schemes such as weighing by substitution, etc.

30. **Weighing Crucibles.** Crucibles whether of platinum or porcelain should be thoroughly cleaned, rinsed with distilled water, dried, heated to redness and cooled (26, 2) in a desiccator before they are weighed. The best method of drying is to set the crucible in a triangle and heat it directly with a Bunsen flame. In the case of porcelain this must be done carefully by holding the burner in the hand and brushing the flame across the crucible till the water is all driven off. After the heating the crucibles are to be handled only with the tongs. When a hot porcelain crucible is to be lifted, the tongs should be warmed. Crucibles are weighed before every analysis, and in case a lid is required (33) the two are weighed together.

31. **Weighing Glass Vessels.** Unless the method of weighing by tares (28) is employed, large glass vessels, after being cleaned, are best wiped dry on the outside with a clean cloth and allowed to stand sometime exposed to the air but protected from dust before they are weighed. It sometimes happens that dry glass when wiped

with a dry cloth becomes electrified to such an extent as to affect its apparent weight. Twenty to thirty minutes are required to dissipate such a charge. The error due to condensation of moisture on the large surface (26, 3) exposed is less than if the glass were placed in a desiccator. A clean cloth makes the best cover to keep off dust.

**32. Use of the Weighing Bottle.** Many substances through loss of water vapor or some other volatile constituent or by absorbing water vapor from the air, change in weight so rapidly that special measures must be used in handling them. When such substances are to be weighed out for analysis, a portion is put into a light, glass stoppered bottle which is then weighed with its contents. The stopper is then removed and approximately the amount desired is poured out into a suitable vessel. Bottle and remainder of contents are again weighed, the difference between the two weights being the weight of the substance poured out. By this method the substance is exposed to the air for the least possible time. If the right amount is not obtained the first time the operation must be repeated. It must be pointed out, however, that the method will apply only to homogeneous material. If particles of different specific gravity are in the mixture the composition of the portion poured out will differ from that which remains.

Liquids can be weighed in these bottles by taking first the weight of the empty bottle, adding a portion of the liquid, closing with the stopper and reweighing. A trick to remember is not to allow any liquid to touch the ground glass parts.

This method for liquids can also be used for unstable powders (37).

**33. Weighing Hygroscopic Material.** It frequently happens that substances that have been dried or ignited are so hygroscopic that before they can be weighed, sufficient water will be taken up from the air to vitiate the experiment. In extreme cases such material is inclosed in glass stoppered weighing bottles but usually the following procedure will serve every purpose: After drying or igniting the material as the case may be its approximate weight is found. The drying or igniting is then repeated and before removing the substance from the desiccator the weights are placed on the pan so that the rider alone need be manipulated to complete the

weighing. In the few seconds this requires no appreciable water will be taken up. The containing vessels should always be covered.

**34. Approximate Weighing.** When, as is sometimes the case (35), a weighing through the fourth decimal place is not required, it in no sense means that carelessness is permitted. An approximate weighing to have any value must be correct within certain limits and these limits must be known. For example, the expression, 1.02 g. is "about a gram," but it is much more definite than that for it means that the weighing is correct within 0.01 g.

When approximate weights are wanted in quantitative analysis the simplest procedure is to weigh to a certain decimal place, that is, stop with the weights of that place. If, in weighing a crucible for example, it is found that 16.43 g. are too heavy and 16.42 g. are too light, it is quite plain that 16.42 g. are correct within less than 0.01 g. Similarly 16.426 g. means by this plan of weighing, heavier than 16.426 g. but lighter than 16.427 g.

Each student should solve the following problem: A sample for analysis is weighed by first weighing an empty vessel, then the vessel plus a portion of the material in question, the difference between the two weights being the weight of the sample. If both weighings are made only to the second decimal place, what is the maximum error which can affect the weight of the sample?

The number of decimal places filled out indicates the degree of accuracy. If significant figures are lacking the necessary number of places should be filled in with ciphers. For example, when making a careful weighing it might be found that 10.4 g. exactly counterpoises the object. The record should, however, read 10.4000 g. since 10.4 g. would mean that the weighing was made only to the first place. 10.40 g. means through the second place, etc.

**35. Required Degree of Accuracy.** All the weighings in the course of the various quantitative operations need not be made to the fourth decimal place and it becomes therefore a practical problem from the standpoint of economy of time to know when this operation can be shortened. An approximate weight (34) will serve if the maximum error that could be introduced does not affect the final percentage result by an amount approaching the allowable error. The simple rule is then, to calculate the error in weighing to

percentage of the constituent sought. For example, suppose three grams of an ore containing 0.54% phosphorus were taken for analysis and weighed only through the second place. An error of 0.01 g. could be made. 0.01 g. is 0.33% of 3 g. and the final result will therefore be affected by 0.33% of its value. 0.33% of 0.54% is 0.0018%; an amount entirely negligible. On the other hand when the precipitate of  $Mg_2P_2O_7$  is weighed an error of 0.01 g. would represent 17% of the whole, thus showing plainly that the weighing in this instance must be accurate.

In the determination of barium in barium chloride, where four tenths of a gram are taken for the analysis, an error of 0.01 g. would be 2.5% of the whole amount. 2.5% of 56%, the percentage of barium in the chloride, is 1.4%. An error of 0.001 g. in weighing the sample would be 0.14%. This latter, while within the degree of accuracy required, 0.30%, is nevertheless too large a part of it, and should not be allowed. In this connection see also section 77.

The student is urgently recommended to calculate in the case of each practice analysis what the allowable error of weighing would be. In this way he will become familiar with a very important phase of quantitative chemical measurement.

**GRAVIMETRIC ANALYSIS.**

The successive operations of a gravimetric analysis are as follows: (1) preparation of the sample; (2) weighing the sample; (3) solution of the sample; (4) precipitation; (5) filtering and washing the precipitate; (6) igniting the precipitate and (7) weighing the precipitate.

**The Sample.**

36. **Preparation of the Sample.** It is obvious that the small portion used in the actual analysis should represent an average of the larger commercial quantity such as the car load, cargo, etc., which the final result is intended to describe. The operation of preparing this small portion is called sampling, and it may be considered as important as the analytical work itself, since an analysis would be of doubtful value that represented nothing more than the gram portion that was used in obtaining it.

An extended description of the art of sampling is seldom if ever included in an elementary course, but its general principles should be known even by the beginner, so that when a situation demanding it arises, it will be recognized and more complete information obtained from suitable sources.

The one guiding principle is to select the small portion in such a way as to make it an average of the larger lot. The best illustration perhaps that can be given, is the method of sampling a pile of loose material such as ore or coal, in which the particles differ greatly in size and composition. This method is briefly described below to give an idea of the painstaking work required to obtain a reliable sample.

The pile is gone over in a systematic way and at regular intervals a shovelful is taken, coarse or fine as it may come. These shovelfuls are thrown together in a clean place, the larger lumps are broken up and the whole pile thoroughly mixed by shoveling over. The pile is then shaped into a flat cone and divided into quarters by cutting it through along two diameters at right angles to each other. Two diagonally opposite quarters are now selected, the other two being discarded. These are combined, extra large

lumps broken, and the pile mixed and quartered as before, this process being continued till a pile of a bushel or so is left with no piece in it larger than a hen's egg. A sieve of about one inch mesh is now brought into requisition and all lumps failing to pass are further crushed. The process of mixing and quartering is then performed a couple of times and the remaining portion further crushed till it will pass a  $\frac{1}{4}$  inch mesh. Mixing and quartering are again taken up, using a smaller mesh sieve from time to time till a portion of 50 to 100 grams has been put through a sieve of 60 to 80 meshes to the inch. This is then bottled for use.

The above operations are usually conducted in two stages, the first being carried out where the large lot is located and when the selected portion has been reduced to a convenient size it is sent to the chemist who continues the sub-division in the laboratory with the spatula instead of the shovel as a mixing tool.

Metals are sampled by drilling into various parts of the piece so that every side shall be represented, and then mixing and quartering these drillings if necessary. In many cases such samples are greasy from the oil used in boring, in which event they should be washed with alcohol and finally with ether. If the piece is a rough casting, adhering slag must be removed where the drilling is done.

**37. Sampling at the Balance. Weighing the Sample for Analysis.** Even after the final preparation of the bottleful of fine material, several important points remain in the actual weighing of the portion for analysis.

(1). When the material is stable in the air, the whole amount is poured out of the bottle onto a sheet of smooth paper and thoroughly mixed with the spoon spatula<sup>1</sup>. The amount to be weighed is now made up by taking small portions at a time from different parts of the pile and placing them in the watch glass or other vessel in which the substance is to be weighed (24, 3). A spoon spatula should be used instead of a flat one because with the latter a portion would always fall off and this might be of different composition from the rest. With a sharp edged spoon a small amount can be taken up clean. The transfer from the watch glass to the vessel

<sup>1</sup>In the Ohio State laboratories a small, silver spoon provided with a slender wooden handle about four inches long is part of the quantitative outfit.

in which the sample is to be dissolved must be done carefully to avoid loss, especially if the material is dusty. The main portion can be poured off gently and all but the last traces removed by tapping the glass. These traces are recovered by means of a soft brush. Two important points, however, are to be noted in its use: It must first be cleaned by striking the bristles and after brushing a sample from the watch glass any adhering matter must be shaken out by striking it against the side of the receiving vessel.

If the weighed sample is to be transferred to a flask, a piece of glazed paper is cut into the form of an elongated V and folded along its length into the shape of a trough. The flask is then set in an inclined position with this paper trough inserted in the neck. The projecting, broad end serves to receive the sample which is then transferred by righting the flask and tapping and brushing the paper. The neck of the flask must of course be dry.

(2). When the material is not stable in the air the method of weighing from a weighing tube or in a closed vessel (32) must be used.

(3). In the case of many kinds of ores or rock material in general it is necessary to grind the portion used for the analysis in an agate mortar so that it will dissolve readily. In using the mortar this point should be noted; only a small portion at a time should be put into it. This can be ground fine in a minute or so after which another small portion is taken, and so on till sufficient is obtained for the analysis.

(4). It sometimes happens that the material is of such a nature that it can not be pulverized to a fine powder. The best preparation possible leaves it so coarse that a small amount can not be taken that will be representative of the lot. In such a case a large amount, 5 to 10 grams, is weighed (35). This large portion is dissolved and the solution diluted to a definite volume in a graduated flask. It is then thoroughly mixed by stoppering the flask or closing it with the thumb or ball of the hand, and alternately inverting and righting it a number of times. From this now, an aliquot part representing the desired weight of sample can be taken by means of a pipette which, however, must first be rinsed with 10 to 15 cc. of the solution before the portion to be used is measured from it. If the instruments are not calibrated, their relation to each other should be established by measuring into the dry

flask the appropriate number of pipettefuls of water and marking the level of the liquid on the neck. (For details regarding the use of flasks and pipettes for accurate measurement, see sections 85 and 86.) Since a solution is perfectly homogeneous and the volume measurement can be made with a high degree of accuracy, this method by dividing the errors becomes a very accurate one. By its use even unstable material can be weighed in the ordinary manner.

(5). The question as to whether a certain convenient amount as 1 g. or 0.5 g., etc. should be weighed, or whether approximately the correct amount (40) be taken and then its weight determined accurately, is one that must always be considered. In the first case after the watch glass or other receiving vessel has been counterpoised, weights to the amount desired are placed on the right and then portions of the sample added on the left till equilibrium is obtained. With finely powdered, stable material the operation is relatively easy by adding or taking away, as the case may be, minute portions after the approximate amount has been found. Obviously the plan can not be used with material that changes in weight rapidly in the air. The second method calls merely for putting approximately the correct amount (40) into a counterpoised watch glass or other vessel and then weighing it. It is the only plan that can be used with the weighing tube (32).

The first method takes more time and is not as accurate owing to the longer exposure of the sample to the air. It would scarcely be used in very exact work. (See however 37, 4). Its advantage lies in the great saving of calculation and consequent chance of mistake when working with a weight of sample like one gram, as compared with a weight like 1.0742 g. The laboratory note keeping is also simplified, for when exactly some definite weight is added on the right there is no advantage in entering the weight of the vessel in which the sample is being weighed. Its weight indeed need not be known. It needs only to be counterpoised. The weights added must be read accurately and checked (24) and constitute the only entry that need be made in the note book.

(6) Factor Weights. The advantages of using a certain definite weight of sample can be increased when such an amount is taken that the weight of precipitate obtained will give directly the percentage sought. This eliminates all calculation and in a com-

mmercial laboratory where many analyses are made, the time and chances of mistake saved, make it a scheme of great value.

The calculation of the final percentage result in a gravimetric analysis is as follows:

$$\frac{\text{Weight of Precipitate} \times \text{Factor}}{\text{Weight of Sample}} \times 100 = \text{Percentage.}$$

Factor, in the above formula is the relation by weight between the precipitate and the amount of the constituent sought. For example, in Practice I. where barium is determined by weighing it in the form of barium sulphate, the factor representing the amount of barium in the sulphate is 0.5886, found by solving the expression,

$\frac{\text{Ba}(137.43)}{\text{BaSO}_4(233.49)}$ . It is clear that if the weight of sample can be made numerically equal to the factor, the two terms will cancel, and all that remains will be the multiplication of the weight of precipitate by 100, or moving the decimal point two places to the right. The factor weight is therefore the weight in grams numerically equal to the factor for that particular calculation. In the case of Practice I. if 0.5886 g. be taken the weight of barium sulphate obtained will give the percentage of barium, merely by moving the decimal point.

It sometimes happens that the factor weight so obtained is too small (40). In this case it is multiplied by some small whole number which must be taken into account in the final calculation. For example, the factor for S in  $\text{BaSO}_4$  is 0.1373. 0.1373 g. is, however, too small an amount to use and consequently should be multiplied by 5 at least. After moving the decimal point in the weight of the precipitate, it is further divided by 5 to get the true result.

Another variation of factor weight is discussed under volumetric analysis 101,5 and 107,7, where the weight of sample is so adapted to the strength of the standard solution that the volume used gives the percentage directly. For a combination of the two see General Note, page 199.

**38. Water in Samples.** Water exists in substances in two forms, as hygroscopic water or moisture and as combined water. The former is driven out by drying the sample at 100 to 110°. The latter is held in chemical combination as water of crystalliza-

tion or as hydroxyl and no definite temperature can be given for its expulsion. Some forms are given up on exposure to the air, while in other cases prolonged heating over the blast lamp is required.

The effect on the integrity of the sample lies in the uncertain and changeable amount of the hygroscopic water or moisture. To obviate this it is customary to report the analysis on the basis of the dried material. Two plans can be used: Either the sample can be dried and a portion of this dried material used for the analysis, or the moisture can be determined in a separate portion and the analysis calculated to the dry basis. The latter is to be preferred because it frequently happens that the substance after drying absorbs water again from the air so rapidly as to make its proper preservation in the dry state almost impossible.

39. **Determination of Moisture.** No absolutely general rule can be given. There is no sharp, dividing line between moisture and combined water. Many kinds of material begin to decompose at  $100^{\circ}$  and some gain in weight by taking up oxygen from the air. Each kind is a law unto itself and the method of treating it must be looked up in its special literature.

Drying the sample to constant weight (59, 5) at  $100$  to  $110^{\circ}$  is the most nearly general rule that can be given and is the one almost universally followed for that large class of inorganic material represented by ores, clays and rocks. The exact temperature, so long as it falls between the two mentioned, is not of great importance. The best plan, especially when no temperature regulator is at hand, is to attempt to hold the drying oven at  $105^{\circ}$ , which can easily be done within one or two degrees by regulating the height of the gas flame.

40. **The Amount of Sample to Weigh.** The general considerations governing this point are as follows:

(1). A small amount of sample, such as 0.5 g. or less, is easily dissolved and the precipitates from it are small in bulk and therefore easily washed and otherwise treated. On the other hand all errors of weighing, the inevitable slight gains and losses in the course of the analysis, etc. are large percentage errors.

(2). Large amounts of sample are more difficult to dissolve and in case the percentage of any constituent is high, the bulk of the precipitate will make it difficult to handle. The advantages are,

that owing to the large amount of material used the errors of weighing, etc. are relatively small.

The student is urged to make a number of calculations such as those in 35 and 78.

41. **Solution of the Sample.** The method of solution is of course conditioned by the character of the material composing the sample, and must be learned for each case. Certain points, however, are general in their application and should receive especial attention.

(1). When the sample is to be dissolved in acids, or indeed in any solvent, by the aid of heat the beaker should be covered with a watch glass convex side down and the boiling should be only sufficient to keep the material well mixed. Rapid boiling would result in rapid evaporation with consequent loss of solvent.

(2). In some cases there is more or less effervescence due to escape of carbon dioxide or other gas which would carry out enough of the solution in the form of spray to affect the results. Such samples are first covered with water and the acid added in small portions at a time. To prevent loss by spray the solution may take place in a flask in which is set a funnel through which the acid is added; or in a beaker or casserole covered with a watch glass, the acid being added through the lip by means of a pipette, the tip of which must then be rinsed off. If the effervescence is not too violent the watch glass can be drawn aside and the acid poured in through the lip. When the action is over, funnel or watch glass, as the case may be, is to be rinsed off into the vessel. If the mixture is to be evaporated as is often the case, the watch glass must remain in place till the gas is all driven out of the solution, after which the under side is to be rinsed off before removing it. The above manipulation will also apply to the addition of acid to any solution containing a carbonate. (See (4) below.)

(3). Special methods of solution are described under Determination of Nitrogen and Determination of Sodium and Potassium. A point of quite general application to rock material is, that simple ignition over the blast lamp greatly increases the solubility in acids. In the case of carbonates care must be used to prevent loss by a too rapid evolution of gas.

(4). Fusion in Sodium Carbonate. As a general rule clays and rock material are not entirely soluble in acids and other methods must be employed. Of these, fusion with sodium carbonate is the most frequently used, its efficiency depending on the higher temperature (red heat) obtained and the different chemical action of the liquid carbonate. Practically all ores, rocks and clays contain quartz and silicates which are insoluble in acids. These are acted upon by the melted salt with the formation of sodium silicate and aluminate which are soluble in water. Other metals present in the sample form new silicates and carbonates, all of which are soluble in dilute acid. The net result therefore of the fusion, is to produce a mixture which is entirely soluble.

Sometimes in the case of material which is very little acted upon by acid such for example as clay, the whole sample is fused. In other cases as in limestones and iron ores only the part insoluble in acid is so treated. The advantage of first dissolving a portion with acid is, that much less of the sodium carbonate need then be used, thus introducing less foreign material into the analysis.

The following detailed description of the method of making a fusion is of general application and may be used wherever such fusion is called for. Some authorities recommend the use of various mixtures of sodium and potassium carbonates or sodium carbonate with acid potassium carbonate. The only advantage these mixtures have is that they melt at a lower temperature than the sodium carbonate alone. When, however, a blast is at hand the higher melting point of the sodium carbonate is an advantage. The anhydrous salt is used.

The material to be fused, the original sample or the residue left after treating it with acid as the case may be, is mixed in a platinum crucible with five or six times its weight of the carbonate. The crucible is then covered with a tightly fitting lid and set in a triangle over a Bunsen burner where it is heated slowly at first and finally with a full flame. The lid may be lifted from time to time and when no more effervescence is observed the crucible may be carried to the blast lamp where it should be heated five to ten minutes. The sign of sufficient heating is the absence of any noticeable effervescence in the melted mass. It usually, but not always, looks clear when the action is over. During the heating the blast flame should be directed obliquely against the lower part of

the crucible. When the operation is complete the crucible is grasped with the tongs — the tips must be clean and bright — and so turned and inclined as to cause the mass to flow over the sides where it quickly solidifies in a thin sheet. As soon as it becomes solid and while it is still red hot the crucible is dipped into cold water. This sudden chilling greatly facilitates the subsequent removal of the mass. (Red hot platinum may be grasped with clean metal tongs not platinum tipped provided the crucible is not held in the flame. The tips so rapidly cool the part touched that there is no danger. If the crucible is to be held in the flame, however, the tongs must be provided with platinum tips.) When the crucible is cold the contents are removed to a suitable vessel such as a beaker or casserole, the last traces being dissolved out with dilute hydrochloric acid. The under side of the lid must also be washed off into the vessel. The successful removal of the hard cake resulting from the fusion requires skill. As a rule it can readily be pried loose from the sides with a thin piece of hard wood, a tooth pick, but on no account should any hard metal tool be used for this purpose as it quickly ruins the soft crucible. If the above plan fails, heating a little water in the crucible is worth trying. As a last resort the crucible can be laid on its side and covered with dilute hydrochloric acid in which the cake can be allowed to digest till dissolved. In any event this plan should be followed when the fusion has been made at the end of the day, as the operation of digestion can then go on during the night with a great saving of time. Another neat scheme is recommended by Talbot. The fused mass is allowed to remain in the bottom of the crucible and while cooling, a platinum wire coiled so as to hold firmly is inserted. The mass is allowed to solidify and is immediately reheated sufficiently to loosen the cake which is then lifted out by means of the wire. In any event, after the contents of the crucible have been transferred, the vessel is covered with a watch glass and an excess of dilute hydrochloric acid added (41, 2). The action of the acid on the excess of carbonate is rapid at first but becomes slower as a film of silicic acid forms on the lumps. This should be removed from time to time by stirring. When all hard particles have disappeared, the solution of the sample is complete and may now be used for any appropriate analysis. In many cases a greater or less amount of silicic acid may have separated, but this can be recognized by its soft, flocculent appearance. The test for a suc-

cessful fusion is to explore the bottom of the vessel containing the solution with a stirring rod. No gritty particles should be felt.

### Precipitation.

**42. Practical Points.** (1). The size of the beaker in which the precipitation is to be made must be adapted to the volume of solution. From two thirds to three fourths full is a good rule.

(2). Before adding the reagent the conditions for the precipitation in hand should be reviewed. Is the concentration of the solution right; is it at the proper temperature; is its reaction (acid or alkaline) right; have the proper additions, as ammonium chloride, for example, been made; what excess of reagent is to be used and at what rate is it to be added? These are all questions to be answered before proceeding with the work.

(3). The precipitant is added in solution, usually quite slowly, drop by drop. It is accomplished best by using a pipette, but when several precipitations are to be made or the rate of addition is very slow, a burette is more convenient.

(4). In order to insure thorough and prompt mixing, the solution must be stirred during the addition of the precipitant and for some time afterwards. There is an art in this stirring that must be learned. The trick of it is to let the rod strike the *top* of the beaker, *not the sides below the liquid*. Practice with water in a beaker. If that breaks there is at least no loss of time previously spent on the analysis.

(5). The manipulation involved in dissolving and reprecipitating (48, 7) may take either of two forms: (a) The precipitate is washed once or twice on the filter and is then transferred to the beaker in which it was precipitated by inverting the funnel and washing it out of the paper with a stream from the wash bottle. It is then dissolved in the appropriate solvent, the proper excess of precipitant is added and reprecipitation brought about. The second filtration must take place in the original filter for some of the precipitate will yet be adhering to it and must not be lost. The principle on which this scheme is based is the well known one of reducing an error to a point where its effect is no longer measurable. In the extreme case of the precipitate containing 1%

of impurities and supposing that 1% of the precipitate is left on the filter, the amount of impurity thus escaping would be 1% of 1% of the total weight of precipitate. This, if the precipitate weighed one gram, would be only 0.0001 g. an entirely negligible quantity in work of this kind. If by chance the filter is damaged it must be treated with acid and washed with hot water to remove any trace of precipitate after which it is to be thrown away. (See (b) below.)

(b). A more exact method is to dissolve the precipitate on the filter allowing the solution to run through into the beaker in which the precipitation was made. The filter is finally thoroughly washed with water and discarded. In carrying out this plan it is well to have an extra beaker at hand which can be substituted for the original one under the funnel after a certain amount of the solvent has been poured through. This first portion can then be poured through the second time and so on till no more precipitate will be dissolved. This enables solution to be effected with the use of a minimum amount of solvent. Acid that is to be poured through a filter should be diluted with at least an equal volume of water.

The question as to which plan is the better is purely one of conditions. When the precipitate is large and of a character that does not dissolve rapidly the first method is to be preferred. On the other hand if the precipitate is very small in amount or very readily soluble the second plan is the better. It is recommended for instance in the case of magnesium ammonium phosphate.

(6) In the estimation of the proper amount of precipitant to add in a given case, advantage is taken of various circumstances. For instance in the precipitation of barium with sulphuric acid, a large excess introduces no source of error and is therefore used. In the case of silver chloride, a change in the physical appearance of the solution indicates the presence of an excess and with the precipitation of ferric hydroxide the odor of ammonia shows that sufficient has been added. None of these is possible when precipitating barium sulphate with an excess of barium. A very large excess is to be avoided and there is no physical change of which advantage can be taken. In this and other cases of a similar kind the chemist must make a rough estimate of the amount present. Several considerations will aid in this: (a) No sample has more

than 100% of any constituent so the weight of sample taken is the maximum possible. (b) The amount of other constituents is sometimes known. This at least is to be subtracted. A salt that has, for instance, 20% of iron can not have more than 80% of anything else. (c) Other constituents may be known to be present in large amount though no determinations have been made. This would further reduce the possible amount of the one sought. (d). The bulk of the precipitate and the rate of its formation when precipitation is begun will indicate the presence of much or little. (e) In some determinations the substance is first separated in a form which is then dissolved and reprecipitated in a different form. The bulk of the first precipitate then gives some information as to the amount present. The determination of phosphorus is an example of this. (f) In the case of reagents with characteristic odors, such as ammonia, which is so frequently employed, the sense of smell can be used to determine the presence of an excess. A certain orderly procedure must, however, be followed. If immediately after adding such a reagent the beaker be placed to the nose, an odor will surely be noticed, but it may come from the unabsorbed gas above the liquid. To make the test properly, the beaker must be removed from the immediate vicinity of the reagent bottle and its contents stirred vigorously for a few seconds. Any fumes that may remain in the upper part are now blown out with the breath; the liquid is again stirred and if then an odor is detected, it may be assumed to come from the excess of reagent in the solution. This use of the lungs as a source of compressed air is sometimes objectionable on account of the introduction of carbon dioxide which, in alkaline solutions, would precipitate the metals of the calcium group. The procedure in (g) below must then be followed. (g) When acid or alkaline reagents are used a piece of litmus paper about an eighth of an inch square can be put into the solution and when its change of color indicates an excess, it should be removed by drawing it up onto the side of the beaker by means of the stirring rod. It can then be held in that position and washed with a stream from the wash bottle after which it is discarded.

(7) Finally, when on the basis of the above considerations, the amount of reagent has been estimated and, together with the appropriate excess (45, 2), has been added, and the solution has stood a sufficient length of time for complete precipitation (45, 6);

*the following test must always be made before filtration:* To a small portion of the clear liquid more of the precipitating reagent is added and if no cloudiness appears on standing, the precipitation may be considered complete. If, however, this test portion becomes cloudy, it must be added to the main solution together with more reagent. The whole is then stirred and, after sufficient time of standing, the test is repeated.

The test portion of 5 to 10 cc. may either be withdrawn from the clear, supernatant liquid by means of a pipette or the first portion of clear solution obtained on beginning the filtration can be used.

**43. Beginning of Precipitation. Solubility Product.** A precipitate will not form till there is present more of it than the given volume of liquid can hold in solution. (See however 44.) Tables of solubilities give little information to the analytical chemist because they refer to pure liquids, whereas the liquids in which precipitations are actually made are solutions of various salts and often strongly acid or alkaline. There is, however, one condition common to analytical solutions and of such pronounced influence on the solubility of precipitates that it has received special study. This is the presence of an excess of the precipitating reagent, the effect of which is to reduce the solubility of the precipitate. For example, if 2.4 mg. of barium chloride were dissolved according to the conditions of Practice I., in 150 cc. of hot water plus 10 cc. of strong hydrochloric acid, and if then 1 mg. of sulphuric acid were added, no precipitate would form, although the Ba and SO<sub>4</sub> are present in the right proportions to react and form 2.3 mg. BaSO<sub>4</sub>. The reason is, that the hot, acid solution is capable of dissolving this amount of BaSO<sub>4</sub>. If now a progressive addition of sulphuric acid be made, 0.5 mg. at a time, with intermediate stirring and several hours standing after each addition, a precipitate will presently form. If this be filtered and more SO<sub>4</sub> added to the clear solution, more precipitate will form and so on till the possible 2.3 mg. BaSO<sub>4</sub> are exhausted. A variation of the experiment would be to have a number of solutions as above, containing different amounts of Ba, say from 0.2 mg. to 2 mg. of the chloride. It would be found that much more SO<sub>4</sub> would be necessary to cause a precipitate in the solutions containing the smaller amounts than in the others. In other words, as the concentration of the Ba decreases, that of the SO<sub>4</sub> must increase in order to bring about precipitation.

This relation which is true of all analytical precipitates has been studied by the methods of physical chemistry and it has been found that as the concentration of one constituent decreases, that of the other must increase at the same rate. In the example above, if the concentrations of Ba and  $\text{SO}_4$  were found at which precipitation just begins and then another experiment were arranged with all conditions the same excepting that only half as much Ba were present, it would be found necessary to use twice as much  $\text{SO}_4$  to start precipitation. In other words, if the concentrations of the Ba and  $\text{SO}_4$  are measured in mols (102,2), the following expression will hold:  $\text{Conc. Ba} \times \text{Conc. SO}_4 = \text{Constant}$ . This means that in a saturated solution or one in which precipitation is about to begin, if more  $\text{SO}_4$  be added, enough  $\text{BaSO}_4$  will at once precipitate to keep the relation constant. This can be generalized, so that by calling the concentration of one constituent of a precipitate A and that of the other B, the formula,  $A \times B = \text{Constant}$ , will be true. This constant is known as the solubility product<sup>1</sup>. It will have a different numerical value for each precipitate.

44. **Supersaturation.** All precipitates, perhaps, exhibit this phenomenon of supersaturation or the tendency not to separate in the solid form till much more is present than the amount conditioned by the normal solubility. In certain precipitates, however, notably in magnesium ammonium phosphate and acid potassium tartrate, this tendency is so highly developed as to require special mention. Vigorous stirring and rubbing the sides of the beaker with the rod should be tried when these precipitates fail to form. It should be added that when precipitation once starts, it proceeds till the solution is normally saturated. The introduction of a minute crystal of the salt in question is a sure method of breaking up the state of supersaturation but obviously must be used with caution in quantitative work.

45. **Completeness of Precipitation.** (1). This means not absolute completeness which is theoretically impossible, but such a degree of completeness that the amount remaining in solution is a negligible quantity. To attain this degree, the chemical nature of

<sup>1</sup>A more rigorous discussion of the solubility product from the standpoint of the dissociation hypothesis can be left to the advanced courses. It will suffice at this point, in the opinion of the author, if the student grasps the simple fundamental fact, that the more dilute the solution of substance to be precipitated, the more reagent must be added to start precipitation.

the precipitate is the largest factor to be taken into consideration. Only those which are relatively insoluble are available. Lead chloride is for instance precipitated by hydrochloric acid, but not quantitatively. In no way can a complete separation of lead be made by this precipitation. Few if any compounds are, however, so insoluble in the ordinary analytical solutions, often strongly acid or alkaline, that they can be precipitated completely by adding just the theoretical amount of reagent.

(2). Fortunately, as seen from the facts brought out in 43, the presence of an excess of the precipitating reagent so reduces the solubility of the average analytical precipitate that the amount remaining in solution is negligible. If 0.200 g. Ba is to be precipitated, much more than sufficient sulphuric acid to react with it must be added. It should be noted that this excess does not react with the Ba. Only the amount calculated according to the chemical equation can do that. The point is, that the calculated amount will not react quantitatively unless more is present. This effect of the mere presence of an excess of one of the constituents of a reaction is called mass action. It is the most important condition in securing completeness of precipitation and explains the constantly recurring direction to use an excess of the precipitant.

(3). The temperature of the solution, though more a factor in the rate of precipitation, nevertheless sometimes exerts a controlling influence on its ultimate degree of completeness. As a general rule substances are more soluble in hot than in cold solutions. There are numerous exceptions, however. Among quantitative precipitates aluminum basic acetate must be kept in a hot solution to bring about complete separation. It is largely a function of the chemical character of the precipitates. The temperature coefficient of some is higher than that of others. This is best illustrated by the case of lead chloride the precipitation of which is almost quantitative in cold solutions when a large excess of chloride is present; but in hot solutions no possible excess will even approach complete separation. In the great majority of cases the solvent effect of high or low temperature is more than offset by the mass action effect of an excess of precipitant. (See 50.)

(4) The volume of solution in which the precipitation is made also affects its completeness. Other things being equal, 500 cc. of any solution will dissolve just twice as much as 250 cc. of the

same solution. It is in the interests then of completeness of precipitation to keep the solutions of as small bulk as possible. (See 48, 7.)

(5). The presence of other salts is also necessary in the case of colloidal precipitates. Arsenous sulphide for example, will not precipitate with hydrogen sulphide unless the solution contains some acid or salt. This is due to the tendency of such substances to form pseudosolutions, half-way solids showing to the eye absolutely no division into separate particles and running through even the closest grained filters. In the presence of salts, acids or bases these pseudosolutions precipitate. Higher temperature also favors such precipitation, this being the reason of the peculiar behavior of aluminum acetate above. For the same reason such precipitates must be washed with a salt solution and not with pure water.

(6). Finally, time of standing after adding the precipitating reagent and the amount of agitation or stirring, plays an important role. Other things being equal, the longer the time of standing and the greater the agitation the nearer completion will be the precipitation.

46. **Rate of Precipitation.** (1). This is an important item since the possibility of saving time enters in. Under exactly similar conditions of concentration, temperature, etc. different precipitation reactions proceed at greatly differing rates. This is due to the different chemical characteristics of the reacting substances. With the same substances, however, the rate of precipitation can be influenced to a large degree.

(2). It is accelerated by increase in temperature, by increase in concentration, by agitation or stirring and by the presence of positive catalytic agents. It is retarded by decrease in concentration, by insufficient stirring and by the presence of negative catalytic agents.

(3). The effect of changes of temperature on the rate of precipitation is a complicated one because the formation of a new compound and its separation in the solid state, precipitation, are not always governed in the same way by the same conditions. Chemical action is perhaps always accelerated by increased temperature but the solvent action of the solution may also be increased to such an extent that it can no longer be compensated by the mass action effect of the excess of precipitant. (See 45, 3.)

(4). The readiest means, however, of changing the rate of precipitation, is to change the concentrations of the reacting substances. The general rule is, that the rate is proportional to the concentration. If equal volumes of a sulphate solution and one of a barium salt be mixed, a certain amount of barium sulphate will form in a minute. If the experiment be repeated, using the same volumes of solution but having that of the barium salt just twice as strong, the rate of formation of the sulphate will be doubled. The same would be true if the concentration of the other salt were doubled. If both concentrations are doubled the rate is multiplied by four. In analytical chemistry, however, rates of precipitation are expressed not so often by amount forming in unit time, as by time required for the complete precipitation of a given amount. The same rule will hold in a general way. The more concentrated the solutions the sooner will the substance be precipitated. The substance to be precipitated should be in as small a volume as possible and a large excess of precipitant used to effect precipitation in the shortest time. (See 50.) The concentration of the precipitant is measured after its addition to the other solution, since in its own solution it may be concentrated, but is of course greatly diluted on being added to a beakerful of liquid.

(5). The effect of agitation or stirring on the rate of precipitation is also very great, being due to the more intimate mixing. In some laboratories where work must be rushed, precipitations are made in flasks which are then put into a shaking machine for five or ten minutes, in this manner accomplishing the same result that would be obtained in an hour's standing.

(6). The catalytic effect of substances in accelerating or retarding the rate of precipitation has been but little studied. Titanium salts are known to retard the formation of the so-called yellow precipitate in the determination of phosphorus.

47. **Purity of Precipitates.** (1). Precipitation may be complete with regard to the constituent sought; but the precipitate may be of such a nature that under the conditions of washing, igniting, etc. it can not be brought to a definite form on which calculations can be based. An illustration of this is the separation of phosphorus by precipitation with ammonium molybdate. The yellow precipitate contains all of the phosphorus but it lacks definiteness of composition. There will be slightly different amounts

of phosphorus depending on slight variations in the methods of precipitation. This is the reason for dissolving it and reprecipitating it in another form.

(2). A precipitate also must be pure, that is, not contaminated with other substances to such an extent as to affect its weight. Complete or partial co-precipitation of other substances must be avoided. In special cases two substances are obtained together and then one of them removed by a special washing solution (see Separation of Sodium and Potassium page 201) but this is the exception.

48. **Adsorption.** (1). A special case of contamination of precipitates exists and is of such general occurrence that it needs separate mention. If a soluble barium salt be added to a solution of copper sulphate the barium sulphate formed will be found contaminated with copper in a form that can not be washed out; yet barium ordinarily does not precipitate copper. Barium chloride could be added to a solution of copper nitrate for instance, and no trace of precipitate would form. When, however, barium sulphate forms in a solution containing other salts these salts will be absorbed to a slight extent by the sulphate, and no amount of washing will entirely remove them. The exact nature of this absorption is not known. In chemistry it is called "Adsorption", the term meaning the carrying down by precipitates of otherwise soluble salts.

(2). Qualitatively considered it is perfectly general. All precipitates show a greater or less tendency to adsorb other salts and all salts in solution exhibit a tendency to be adsorbed.

(3). Quantitatively the degree of adsorption differs greatly. With a given salt in solution some precipitates would be grossly contaminated with it, and others only to a negligible extent. For example, barium sulphate and lead sulphide are both precipitated in hot dilute hydrochloric acid solutions. If potassium salts are present they will be carried down by the barium precipitate to such a degree as to vitiate the subsequent determination of potassium in the filtrate. Lead sulphide, however, though an amorphous precipitate, does not affect the potassium to a noticeable extent.

(4). With a given precipitate and different salts in solution there are likewise great differences in the amount of adsorption. Precipitates in other words show a selective adsorption, taking up

some salts more than others. Potassium salts, for example, are more likely to be adsorbed than are those of sodium.

(5). Amorphous and flocculent precipitates exhibit adsorption more than those which are crystalline, and those which are very finely divided, more than those consisting of larger particles. The explanation of both statements probably lies in the fact that adsorption takes place largely on the surface of solids; therefore anything that increases the surface will increase adsorption.

(6). A relation also exists between the degree of adsorption and the concentration of the soluble salt. Roughly, it is proportional to the concentration of the adsorbed substance; the deviations from strict proportionality being on the side of a relatively lesser adsorption in concentrated solutions. In some cases largely diluting the solution in which a precipitation is to be made will so reduce the concentration as to make it negligible. Usually, however, this is not permissible for other reasons and the following plan, the general application of which is to be noted, is employed when necessary: The precipitate is dissolved and reprecipitated. Since the amount of adsorbed substance is rarely more than a fraction of one per cent. of the precipitate it follows that the solution of the precipitate will be very dilute with reference to this substance; consequently the second precipitation will carry down only a negligible amount of adsorbed material. Since this operation of dissolving and reprecipitating must often be carried out on account of its being a general remedy for the errors introduced by adsorption, some further discussion of it will be of value.

(7). When it is known that a precipitate is to be reprecipitated the first precipitation may be made in a more concentrated solution and with a larger excess of precipitant. These, it is true, are the conditions for maximum adsorption but they are also the conditions for maximum rate and degree of completeness of precipitation, thereby accomplishing a great saving in time. Even under the most adverse conditions the amount of adsorbed salt is not likely to be above a few milligrams so the solution of the precipitate must of necessity be very dilute with reference to it. In other words, at the worst, the solution and reprecipitation will be sufficient purification; so if time can be saved at first it is a point worth noting. Another important point is that when this method is employed there need be no trouble about the right excess of precipitant. In the first

precipitation the amount that would be required if 100% of the sample taken were to be precipitated, together with a large excess as noted above, may be used. When this precipitate is dissolved the solution will of course contain just the theoretical amount of the constituent formerly in the precipitate. The necessary excess can then be measured with any desired degree of accuracy and added. Since the second precipitation corrects the errors of the first, the first precipitate need not be washed more than once or twice. In a few special cases where very fine work is sought, a third precipitation is sometimes made to effect a complete separation from the adsorbed substance. In the case of contamination coming chiefly from the excess of precipitant itself the remedy does not help, excepting in so far as it permits of the exact regulation of the excess required. Occasionally the second precipitation is made with a different reagent as when the volatile ammonium compound follows sodium hydroxide.

(8) The phenomenon of adsorption is also shown by filters, the concentration of the first drops of solution running through being materially less than that of succeeding ones. This point must sometimes be taken into consideration when handling very small volumes of solution. Ordinarily the adsorbed material in the paper is disregarded, thorough washing being depended upon to reduce it. In dissolving and reprecipitating, it is practically eliminated so far as the salts originally present in the solution are concerned, by dissolving the precipitate and discarding the filter.

49. **Physical Character of Precipitates.** (1). The physical character of a precipitate is almost of the same importance as its purity. Its state of subdivision or in other words, the size of the precipitate particles must be such as to permit filtration and washing without running through the filter. Many of the specific directions under the description of any precipitation method bear on this point, therefore its general consideration is of importance.

(2). Some compounds readily separate in coarse heavy crystals and some do not. With the same precipitate the constituent in excess often has a marked influence. This is seen in the case of barium sulphate which comes down in much better form when precipitated with  $\text{SO}_4$  than when Ba is in excess. Magnesium ammonium phosphate is also coarser when Mg is in excess than under the reverse conditions. There is no explanation of this to offer.

It is not characteristic of crystalline precipitates alone for silver chloride shows the same differences.

(3). The presence in solution of substances taking no part in the reaction probably in all cases influences the character of the precipitate. In one or two cases this influence is marked, as is shown by the precipitation of barium sulphate with  $\text{SO}_4$  in Practice I. A large excess of hydrochloric acid favors this precipitation. When the reverse conditions obtain, however, and the precipitation is made with Ba in excess, a large amount of acid causes the precipitate to separate in a finely divided state.

(4). The more slowly a precipitate forms the larger will be its particles, therefore methods of controlling the rate must be studied. This can be done most simply by regulating the rate of addition of the precipitant. The more slowly it is added the more slowly the precipitate will form, which explains the frequently recurring direction to add a precipitant drop by drop with constant stirring. As a rule precipitates forming in hot solutions are in better physical condition than if the precipitation were made in the cold. The solvent action is perhaps the explanation of this.

(5). Digestion in the liquid in which precipitation took place in many instances actually changes the character of the precipitate as well as the size of the particles. Many substances on first separating in the solid form are amorphous but change, on remaining in the solution, to the crystalline form. Possibly all precipitates go through this change but the rate in many cases is so rapid that the amorphous form is never seen. With others it is readily apparent; the rate of change varying at room temperature from a few seconds to hours or more. Higher temperature accelerates this action. The phenomenon is best seen in the case of calcium carbonate. Magnesium ammonium phosphate under certain conditions can be seen first as an amorphous body changing almost instantly to the crystalline form. The corresponding manganese compound requires boiling to produce good crystals.

This change from one form to another is not confined to that from amorphous to crystalline. Changes from one form of amorphous to another and from one crystalline form to another are also common. There is always a difference in the solubility of the two forms, that which first separates being the more soluble. In some cases this difference is so great that the first precipitate will

dissolve readily in a given medium while the second form will not. In such a case it sometimes happens under certain conditions that the second form will, after standing, precipitate from the solution. This is illustrated by the behavior of chromium hydroxide which when first precipitated dissolves readily in an excess of caustic soda but on boiling or after standing twenty-four hours or so at room temperature, reprecipitates. Both precipitates are amorphous but are different modifications of the same substance, the difference undoubtedly being in the degree of hydration. Finally, on digesting or boiling, a precipitate may change entirely in its general composition; as for example when  $\text{Cu}(\text{OH})_2$  is transformed on boiling to  $\text{CuO}$ .

(6). The actual size of the particles of a precipitate is, however, increased by digestion in the mother liquid irrespective of any change in form. If cold solutions of a barium salt and some sulphate be mixed, barium sulphate will precipitate but in a so finely divided state that most of it will run through the filter. If, however, the mixture be digested for some hours on the water bath or boiled for a shorter time the precipitate will be retained without difficulty. The increase in size of the particles of a precipitate under these conditions is due to the different degrees of solubility existing among particles of different size. Small particles are more soluble than large ones. This difference is entirely unrecognizable excepting in the case of very small particles. It has been shown, for example, that barium sulphate in a very fine state of subdivision is 80% more soluble than when the crystals are like those in a good quantitative precipitation.

(7). The mechanism of the change is as follows: A solution in which a solid has separated is saturated with reference to that substance. If there is a difference in solubility among the particles of the solid such that the smaller are more soluble than the larger, then the liquid is saturated with reference to the larger ones only. The smaller ones will dissolve, thus producing a state of supersaturation, to be relieved only by precipitation onto the larger ones. In short the small particles dissolve and reprecipitate onto the large ones. The reason for the greater solubility of the small particles lies in the influence of the surface tension of the film of liquid about them. The surface film of a liquid always tends to assume the smallest possible dimensions. Under ordinary

conditions this tendency is unnoticeable. It is only when this surface energy is matched against an equally small amount of some other form that it becomes apparent. A large amount of water for instance being acted upon by gravity spreads out showing a flat surface. A small drop on the other hand, assumes a globular shape because the relation between extent of surface film and mass of water has been so altered that the surface tension can counteract the attraction of gravity. Obviously if the surface tension can draw the water together against an attraction working in the opposite direction it must exert a pressure on the inside of the drop. This pressure can easily be shown by a soap bubble which always contracts if left on the pipe so the interior is open to the air. Furthermore the pressure exerted by such a bubble is greater the smaller the bubble. This can be shown by an arrangement with a T tube and appropriate cocks so that two soap bubbles can be blown of different sizes and then connected with each other. It will be seen that the smaller will continue to grow smaller and the larger one larger. The greater internal pressure is exerted by the small bubble. If now this internal pressure exerted by a liquid film continues to increase as the film becomes smaller it must of necessity be enormous at the limit of microscopic size. Just as in the case of the drop, so in the case of a solid particle in a liquid, the effect of the surrounding film can not make itself manifest till it is so small that the enormous pressure developed is sufficient to affect the solubility of the solid inside. The size of the film is of course the size of the particle. The film about a small particle exerts a great pressure on it and literally squeezes it into solution.

(8). The question may naturally arise as to how it happens that particles so small as to be soluble ever form at all. In a perfectly homogeneous liquid, they would not; but in the course of a precipitation the concentration of the precipitant is very high at points before it is thoroughly stirred through the whole mass. The mass-action effect of this local high concentration is to precipitate suddenly and therefore in a fine state of subdivision (49, 4) a certain amount which subsequently requires time for its solution. Digestion over some source of heat is more efficient than in the cold because of the continual mixing due to convection currents.

(9). In the case of gelatinous precipitates digestion in the mother liquid causes the flocculent particles to gather together into

larger and denser masses that are more readily filtered. Prolonged boiling causes certain amorphous precipitates to become slimy and difficult or impossible to filter. This is probably in all cases due to the loss of some volatile constituent from the solution rather than to any effect of the prolonged digestion. The physical character of a precipitate is often sharply changed at the point where an excess of precipitant is reached.

(10). In precipitations like that of potassium platinic chloride where the solution is evaporated to dryness, the general rule for obtaining large crystals is to carry on the evaporation slowly, especially from the point at which the separation of the solid begins.

50. **The Balance of Conditions.** In applying the above considerations to practical work in making quantitative precipitations *all* of the effects produced by varying a given factor or set of conditions must be taken into account. As a rule an attempt to push too far the advantage gained by a given factor results in some undesirable effect on the precipitate. For example, a concentrated solution and large excess of precipitant hasten precipitation and insure its completeness. Both conditions, however, if carried too far produce an impure precipitate. Conversely a high degree of dilution favors a pure precipitate but in so large a volume of liquid precipitation may not be complete. Various factors may be combined. The precipitation can be made in a solution sufficiently dilute to insure purity of the precipitate and the solvent effect of the larger volume of liquid counteracted by the proper excess of precipitant. In conclusion the following study-plan is recommended: The student should note the balance of conditions for each precipitate as it is taken up and ask himself a set of questions as to the effect of increasing or decreasing the various factors entering into the method of its precipitation.

#### Filtration.

51. **Filter Paper.** For quantitative work the so-called ashless papers are used. These are prepared by washing a good quality of paper with hydrochloric and hydrofluoric acids, the excess of which is finally washed out with water. This treatment removes practically all of the mineral matter. The weight of the ash left

by the ignition of one filter is printed on the cover of the pack. It is to be subtracted from the weight of the precipitate if the accuracy of the work warrants so fine a correction. Such papers are prepared in different grades according to their closeness of texture. Those designed for retaining very finely divided precipitates are close grained and filter correspondingly slowly. When there is but little danger of the precipitate running through a coarser grained paper is used, thus saving much time. The various grades are often distinguished by the color of the band around the packets.

**52. Funnels.** A good funnel for quantitative work is so made that the angle of the bell is exactly  $60^{\circ}$ . This corresponds to the cone formed by folding a circular piece of paper first on a diameter and second at right angles to the first fold. Cheaper grades of funnels, however, frequently vary from  $60^{\circ}$ , in which case a paper so folded will not fit (53, 2). The stem of the funnel should be about five inches long and small rather than large in diameter, the lower end being ground off at an angle. If the stem of a funnel is too large it does not fill with solution, thereby cutting down the rate of filtration. The filling of the stem is promoted by its being kept free from grease by frequent treatment with cleaning mixture.

**53. Practical Points.** (1). The size of funnel and filter in any case is governed entirely by conditions. The size of the filter is conditioned by the bulk of the precipitate, the ideal relation being such that the precipitate about half fills the filter. If too full, the precipitate can not be washed properly. On the other hand if a precipitate weighing only a few milligrams is in a large filter the action of the carbonaceous matter of the paper is relatively very large, as is also the correction for the weight of the ash. For all but very fine work, however, chemists use but one size of filter selected so that it readily holds the larger precipitates, since the errors introduced by incomplete washing are far greater than those due to the use of a large filter for a small precipitate. The reducing action of the paper during ignition is, in the case of certain precipitates very large, but a special treatment after the carbonaceous matter is burned off is then always used so this, the greatest objection to a large filter, is removed. A 9 cm. filter will be found to meet practically all demands. The relation of

funnel to filter should be such that there is at least half an inch between the top of the paper and the top of the funnel. If the filter nearly fills the funnel the precipitate can not be washed properly. The objection to the use of a funnel much larger than the filter is one almost entirely of convenience.

(2). The filter must be folded so that when wet and pressed down it fits closely without folds or bubbles, at every point excepting perhaps near the bottom. The top especially must be in contact with the glass throughout its whole circumference. This can be accomplished by making the second fold so the edges do not coincide. On opening one or the other part, the angle of the cone so formed will be greater or less than  $60^{\circ}$  and by trial a fold can be found that will fit. Proper washing would be all but impossible if this rule were not followed.

(3). The filter stand holding the funnel should be placed near the front of the desk. The beaker which is to receive the filtrate should be placed so that the stem of the funnel touches the side. This is to prevent loss by spattering. The stirring rod which is left in the solution after precipitation should always be used in pouring into a filter, the stream being directed against the side on which there is more than one thickness of paper.

(4). In many cases precipitates show a tendency to run through. This is likely to occur at first when the pores of the paper have not yet been filled by the finer particles. It is well therefore to have at hand a clean beaker, and if the first 25 to 30 cc. of filtrate appears cloudy it can be poured through again. In most cases the subsequent filtrate will remain perfectly clear. Persistent running through can often be remedied by the use of a closer grained paper. (5) and (5) below.)

(5). The manipulation involved in substituting another paper would be as follows: The first paper is thoroughly washed, folded up as for ignition (60) and laid aside protected from dust. The washings together with the cloudy filtrate are then poured through the second filter. Both papers are finally ignited together. As a rule the small amount of precipitate in the first paper can not be washed off with the stream from the wash bottle, consequently it is best not to attempt it.

(6). Before beginning a filtration, the precipitate is allowed to settle and the supernatant liquid first poured through the filter.

The precipitate can sometimes be washed by decantation (58) before transferring it to the paper. As a general rule, however, the transfer is made at once, the main bulk of it being poured out with the last portion of liquid. Finally the beaker is held in an inclined position over the funnel and the remaining precipitate washed out with a stream from the wash bottle.

At the conclusion of the operation the beaker should be turned over and the outside of the lip washed off. In the great majority of cases all of the precipitate can not be removed by washing alone, as a little will adhere firmly to the sides. This should be rubbed loose by means of the rubber tipped rod, (12) which is then rinsed off and the beaker again held over the funnel for a second rinsing. The small amount of precipitate adhering to the stirring rod must also be rubbed loose. There is more than the usual tendency for the precipitate to "run through" at the time of its transfer to the filter. Beginners will often save time by providing a clean beaker at this point to replace the one containing the bulk of the filtrate. If any precipitate should run through, refiltering of the whole solution will be spared.

**54. Rate of Filtration.** The rate of filtration is of importance from the standpoint of saving time. It is governed by the character of the filter paper and of the funnel, by the temperature and viscosity of the solution and by the character of the precipitate. Coarse grained, crystalline precipitates such as the barium sulphate of the first practice do not clog up the pores of the paper and if the other conditions are right the filtrate runs through in a steady stream. Very finely divided, granular precipitates and especially flocculent precipitates such as silicic acid are liable to stop up the pores of the paper and may reduce the rate of filtration to a few drops a minute. If this happens the student may be sure that there has been some fault in manipulation preceding the precipitation (49). Success in filtration is largely a matter of experience. The older chemist will make the same precipitation that the beginner has tried and on filtering, the solution will run through in a steady stream while the beginner's is dropping ten times a minute. Wherein is the difference? In skill. Quantitative chemical analysis is a question of the trained hand and eye as well as one of weighing and mixing things in a certain order according to the book.

There are various methods of hastening filtration by employing suction but with the exception of the Gooch crucible described below they are not to be recommended excepting in special cases. More time can be saved by proper preparation of the solutions (49) than by using suction afterwards.

**55. The Gooch Crucible.** This exceedingly handy and time-saving appliance consists simply of an ordinary crucible, platinum or porcelain, the bottom of which is perforated with many small holes.

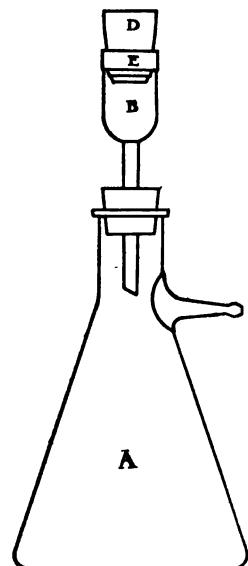


Fig. 3.

A is a thick walled flask especially designed for filtering under diminished pressure. B is a special funnel with straight sides adapted to the size of the crucible D. A tight joint is made by drawing over B a short piece of thin, wide rubber tubing E the projecting end of which is then pushed in. A suitable suction pump is connected with the side outlet of A. For preparing the felt the asbestos and water (see below) are shaken up and enough poured into the crucible to form a layer of proper thickness. The crucible is then set into its support and the suction applied and allowed to continue at least a minute after the water has disappeared. The amount of asbestos to use is largely a question of experience. A fairly good test is,

after removing the crucible with the felt still moist, to hold it towards the light. The outlines of the holes should be just visible.

When the proper amount of felt has been obtained, the crucible is cautiously heated at first, to avoid mechanical loss by spattering, and finally to redness over the Bunsen burner or blast lamp, depending on the subsequent ignition of the precipitate. Even the best asbestos loses a little on blasting so the empty crucible and felt must receive the same treatment as the precipitate. When ready to begin a filtration the crucible is set in place and the suction started before any liquid is poured in. At best, beginners frequently have trouble at this point in preventing the felt from being stirred up. It is, however, a question of experience and skill and soon no trouble will be found.

When the first precipitate has been ignited and weighed, another of the same kind may be filtered on top of it and so on for a number of times depending on the bulk of the precipitates and the good behavior of the felt.

The asbestos often presents difficulty as much of that on the market for the purpose is not good. The best preparation is made from the crude Canada mineral as follows: The fibers after being separated somewhat, are cut into lengths of about a quarter of an inch. This material is then moistened with hydrochloric acid and rubbed in a porcelain mortar to break up the adhering bundles after which it is transferred to a beaker and digested several hours with more hydrochloric acid. The excess of acid is then washed out and the fibers thoroughly broken up by rubbing the wet mass through a coarse sieve. A square of clean "wire gauze" serves admirably for this. Another short treatment with hydrochloric acid should now be given after which the material is thoroughly washed by decantation or on a muslin filter. It is then ready for use and should be kept suspended in water.

#### *Washing Precipitates.*

56. **Solutions for Washing.** Before a precipitate is ready to ignite, it must be freed from the non-volatile salts contained in the original solution with which it is still wet. This is accomplished by pouring through the filter a liquid or solution which has no

solvent action on the precipitate but in which all the material it is desired to remove is soluble. The washing solution must further contain no non-volatile constituents or anything that will interfere with the subsequent determinations to be made in the filtrate. Water is the liquid usually employed though others are sometimes used, as alcohol and ether. Frequently an acid or alkaline liquid or a salt solution is necessary. Since nearly all the common acids are volatile there is almost free choice for an acid wash water. When alkaline or salt solutions are required, the hydroxide or some salt of ammonium must, as a rule, be used.

57. **Practical Points.** (1). When a precipitate is washed on the filter the stream of water or washing solution from the wash bottle should be directed against the extreme upper portion of the filter and occasionally during the operation, the sides of the funnel should be washed down. After carrying the stream around the edge of the paper it is well to direct it into the center, thus "churning" up the precipitate and preventing the formation of lumps which would resist the action of the wash water. In washing, the filter is always allowed to drain completely before adding more water. If some of the last wash water remains, the addition of more simply serves to dilute it and the advantage of a fresh application is impaired to that extent. In using the wash bottle for washing precipitates, a stream is first started and while the tube is full of water, is pinched off. The stream can now be directed into the filter without fear of splashing the precipitate because the water is no longer mixed with air.

(2). Many precipitates show a tendency to creep up the sides of the funnel. No attention, however, need be paid to this as the small amount on the glass is easily removed (60).

(3). There is no general rule for the number of times a precipitate should be washed and *in all cases the washings should be tested* for some substance originally present in quantity. When this is entirely removed it is assumed that everything else is also washed out. It so happens that in the great majority of analytical operations, owing to the use of hydrochloric acid as a solvent, chlorides are present in large amounts. Fortunately the qualitative test for chlorides is both very delicate and very easy to make. This is the reason why this test is the one usually made to determine the completion of washing. Were the washing con-

cerned only with the removal of the original liquid present, three or four times would be sufficient, but owing to the adsorption or condensation of salts, otherwise soluble, on the surface of the particles of the precipitate, washing must be carried very much further. As a rule one may begin to test after the sixth or seventh washing. Often the twentieth will still react for chlorides.

The proper procedure in making the test for chlorides is as follows: A few drops of the nitric-acid-silver-nitrate testing solution (14) are placed in a test tube. If no cloudiness is produced the test tube is proven to be free from chlorides and if now a cubic centimeter or so of the washings are added and a white precipitate forms, it shows the washing to be incomplete. As commonly done, adding the silver solution to the washings, a white precipitate might be due to chlorides in a dirty test tube.

(4) It sometimes happens that adsorbed (48) substances that cannot be washed out of a precipitate under ordinary circumstances are readily removed after ignition. If, therefore, the nature of the precipitate permits, a fairly thorough washing is given followed by ignition. The contents of the crucible are then cooled, transferred to a new filter and again washed, after which the final ignition to constant weight is made. This second washing is easily managed when a Gooch crucible is used.

58. **Washing by Decantation.** Certain precipitates, owing to their gelatinous character, quickly stop up the pores of a filter, thus making the operation of filtration extremely tedious and sometimes impossible. In these cases decantation is resorted to. The precipitate is allowed to settle until the supernatant liquid is clear; then by means of a siphon or pipette this clear liquid is drawn off as closely as possible without disturbing the precipitate. A large volume of the washing solution is now added, the whole is stirred up and again allowed to settle. This operation of drawing off the clear liquid and adding fresh portions is continued until the washings no longer react for the substance it is desired to eliminate. If the decanted washings are poured through the filter it is not necessary to wait until they are perfectly clear. With very gelatinous precipitates, such as aluminum hydroxide, the washing is done best in a beaker of at least a liter in capacity. 800 to 900 cc. of wash-water can then be used at a time.

The most convenient method of drawing off the supernatant

liquid is by means of a siphon which may be made by bending a piece of glass tubing the size of that used for wash bottles. A piece of soft gum tubing about four inches long is put onto one limb so it can be closed by a pinchcock. In using this siphon it will be observed that while running at full stream the clear liquid can not be drawn off closer than about an inch to an inch and a half above the precipitate owing to the strong current bringing up a tiny stream of the precipitate itself. If however, the pinchcock be closed partially so as to reduce the flow through the siphon, it can be brought closer and closer until finally, with the current reduced to dropping, the liquid can be drawn off to within less than a quarter of an inch of the precipitate. A convenient plan is to hold the siphon in a clamp attached to a ring stand and use a screw pinchcock or a wedge shaped piece of wood in the ordinary kind, so that the flow can be adjusted. The upper portion of the liquid can then be drawn off rapidly and by gradually lowering the siphon and cutting down the rate of flow, practically all the liquid above the precipitate can be drawn off without disturbing the precipitate itself. Washing by decantation is not employed if the precipitate is of such a character as to permit of filtration because decantation as a rule requires more time and a much greater quantity of washing solution.

#### **Ignition of Precipitates.**

59. **General Points.** (1). **Kind of Crucible.** When both platinum and porcelain crucibles are available the former is to be preferred. The metal is much more readily heated and cools quicker after the ignition. In some cases, however, the chemical nature of the precipitate will not permit the use of platinum (67). Other situations, as when treatment with hydrofluoric acid is to be used, demand it. It is a question that must be decided in each case.

(2). **Chemical Action of the Filter Paper.** The reducing action of the carbonaceous matter of the paper is such that with some precipitates, as for example, silver chloride, it is not safe to heat the two together. In other cases this tendency towards reduction, while present, may be kept within bounds by allowing ready access of air during ignition. Barium sulphate is an example of this. Many precipitates on the other hand, are unaffected

and the paper may be burned off with no fear of reduction. Examples of this are silica and calcium oxide.

(3). Temperature of Ignition. Some precipitates like silver chloride will not bear a red heat. Others may be ignited over a Bunsen burner but decompose at the temperature of the blast lamp. Obviously the characteristics of each precipitate must be known. The following terms are used to designate temperatures: Short of redness; low redness; full redness; blast lamp. Some precipitates as potassium platinic chloride are dried. In this case the temperature is given in degrees. Occasionally some physical change marks the ignition temperature as when silver chloride is heated just to the fusing point.

(4). Special Treatment. In certain cases after the filter is burned off, the precipitate is treated with some reagent to transform it into another compound more suitable for weighing. The treatment of calcium oxalate with sulphuric acid to change it to the sulphate illustrates this point. The treatment of silica with hydrofluoric acid is an example of a different nature.

(5). Ignition to Constant Weight. Many precipitates lose their volatile constituents so slowly that some test for completion of ignition must be used. It is assumed that when two successive weighings with an intervening period of ignition agree, equilibrium has been attained and no further loss will take place. The successive ignition periods should be at least ten to fifteen minutes. Beginners need not try for absolute agreement in the last two weighings. Differences no greater than 0.2 to 0.3 mg. may be called "constant weight."

(6). Apparatus. The burner should be adjusted so that it gives a clear, blue flame, not too high. The triangle for holding the crucible should be supported on a ring of the ring-stand rather than on a tripod. The latter permits of no adjustment to suit the size of flame. The most efficient heat is when the tip of the flame just envelops the crucible.

60. **Ignition of Precipitate and Filter Together.** The moist filter is folded in such a way that the precipitate is entirely enclosed in which form it is put, precipitate-end up, into a weighed crucible which is then laid in an inclined position on a triangle. It often happens that a thin film of precipitate has crept into the upper

part of the funnel during the washing. This can be recovered by wiping it off with the filter as it is removed. In case of an accident like the tearing of the paper any particles of precipitate adhering to the funnel can be wiped off with pieces of ashless filter paper which should then be added to the rest. Owing to the large excess of water present, great care must be exercised on first applying heat, to avoid mechanical loss by spattering. Two plans may be used: (a) If there is no other work pressing the quickest way is to take the burner in the hand and brush the flame back and forth across the crucible. This gives perfect control of the rate of heating which can be made as rapid as possible so long as spattering does not take place. (b) If, however, other work is at hand, a low flame is put under the crucible far short of the point where evaporation will be too rapid. In this way the water will be driven off in ten to twenty minutes. As soon as the filter and contents are dry the heat is increased to the point where the paper chars and smokes away gradually. If it bursts into flame the burner should be removed till the flame dies out. Another plan for the slow heating of a filter and precipitate is to leave the flame at full height but set so that it burns past the open end of the crucible, perhaps just touching the edge. This slow burning off of the paper is better than rapid heating at first, for often the paper cokes to a black mass which then burns away very slowly, in extreme cases an hour or more being required. During the time the paper is burning, the crucible should be laid on its side in the triangle to give free access of air. When all danger of loss due to the rapid burning of the paper is past and there remain only some charred particles, a lid may be leaned against the mouth of the crucible in such a way as to reflect into it more heat and hot air. This increases the rate of combustion. Other tricks of manipulation that may be employed to hasten the burning out of the last traces of carbon are, pressing the carbon against the hot wall of the crucible with a loop of platinum wire; turning the crucible so that fresh portions are brought to a red heat; removing the flame for a moment which causes an inrush of colder air and, if the precipitate is not affected, increasing the temperature by using the blast lamp. Occasionally, especially with silica and magnesium pyrophosphate, black specks remain even after prolonged heating over the blast lamp. In such cases moistening the precipitate with a few drops of concentrated nitric acid and reigniting after the

excess of acid has been dried off, will sometimes cause the black to disappear. This scheme is of course general for all cases where the chemical character of the precipitate will permit the use of nitric acid. Ofttimes some of the carbonaceous matter will sublime on the upper portions of the crucible. This can be removed by turning the crucible so that the black part comes directly over the flame. Finally when all trace of black is removed, the flame is turned up to give the final temperature required and the heating continued for from five to twenty minutes depending on the nature of the precipitate. In order to hasten the final drying and especially in those cases requiring ignition to constant weight (59,5) any large lumps should be broken up with a stirring rod. Adhering particles can be wiped off, after allowing the rod to cool, with a bit of ashless filter which is then added to the crucible. In the case of those precipitates requiring the final temperature of the blast lamp, the paper is first burned off over a Bunsen burner.

61. **Ignition of Precipitate Apart from the Filter.** A precipitate can never be separated quantitatively from the filter but the great bulk of it can be removed and the small part still adhering will not be affected sufficiently to introduce a large error. In some cases this small portion is given a special treatment as is done with silver chloride in Practice I.

In order to remove the precipitate as closely as possible, it and the filter must first be dried. This may be done in a variety of ways. Filter and contents may be removed from the funnel, laid on a watch glass and covered with a paper cone to keep off dust. This arrangement placed on the steam plate will soon dry. The funnel may be covered with a piece of paper and the whole, properly supported, set over the hot plate or steam plate. If a hot air oven is available the filter may be placed in it. Various other details will suggest themselves to the ingenious student. The point is, to dry it without its becoming contaminated in any way. The drying may take place slowly at room temperature or as rapidly as possible without mechanical loss.

The removal of the precipitate from the paper is facilitated by rolling the filter between the thumb and fingers. Most of the precipitate can then be poured out. A small brush can be used for detaching the remainder but care must be taken to see that no particles remain in the bristles. The inside of the filter can also be rubbed with a stirring rod to loosen the last portions. This rod

is cleaned by wiping it with a bit of ashless paper which is then to be put with the rest.

For the ignition of the paper and subsequent treatment of the ash and combining it with the main bulk of the precipitate, several procedures can be used. (a) The precipitate is placed on a piece of glazed paper where it is covered with a watch glass. The paper can now be burned in the crucible in the usual way (60) after which the bulk of the precipitate is added. If the ash is to receive special treatment it can be done before the addition of the precipitate. (b) Another procedure is to fold the filter loosely and twist a platinum wire about it several times. The ends of the wire can be held in the crucible tongs. The paper is then ignited and held over the crucible so that the ash, if any falls, may be received. The burning of the last traces may be hastened by cautiously bringing a Bunsen flame to bear on it for a few moments, then removing it and repeating the action. This does better than holding the flame on it continuously. When the last trace of black is burned out the ash is added to the contents of the crucible. The bulk of the precipitate is then added or the ash given special treatment as the case may be. If ash and precipitate are to be treated together as when calcium oxalate is transformed to sulphate the precipitate should be placed at once in the crucible and the ash allowed to fall into it.

**62. Treatment with Sulphuric Acid.** This may be looked upon as a special case of ignition. Salts of many other acids can readily be transformed into sulphates by treatment with an excess of sulphuric acid and evaporation to dryness and ignition. Since the sulphates of many of the metals are stable at red heat or like those of iron and aluminum, change quantitatively to oxides, the plan is frequently used.

The point of difficulty lies in driving off the last portions of sulphuric acid without loss due to spattering of the pasty mass. The following procedures are to be recommended: (a) The double crucible method of Treadwell. This consists in placing the crucible containing the moist sulphate in a larger one as shown in Fig. 4. A is a circular piece of asbestos board with a hole cut in the center to carry the smaller crucible. The larger crucible is heated

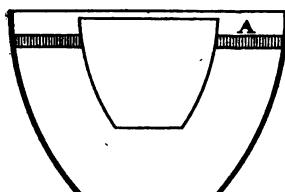


Fig. 4.

center to carry the smaller crucible. The larger crucible is heated

on the bottom with a free flame and serves as a hot air bath for the smaller one. With proper regulation of the heat the excess of acid can be driven off without loss. (b) The other plan requires more skill but is nevertheless not so difficult as it seems. It consists simply in setting the crucible in a triangle and heating it by brushing the flame across the bottom, the burner being held in the hand during the entire operation. This intermittent, momentary application of heat permits of its careful regulation. Turning the flame directly into the top of the crucible is also a good plan when there is no danger of reduction.

63. **Weighing in Tared Filters.** When precipitates are to be dried rather than ignited, preparatory to weighing, and a Gooch crucible is not available, this method should be used. Two ashless papers are dried in the hot air oven at the same temperature and for the same time that is subsequently to be used for the precipitate. They are then weighed by the method of tares (28), the lighter one being on the right. It should be marked "tare" with a lead pencil. Both filters are then placed in the same funnel, the tare being underneath. With this arrangement filtrate and washing solution must pass through the tare filter exactly as through the one containing the precipitate; in other words the conditions are made the same for both filters. At the conclusion of the filtration and washing, the funnel is set in the hot air bath and when the drying is completed, the two filters are separated and the weighing made. This method is especially suited to the weighing of potassium platinic chloride.

*Miscellaneous Operations.*

64. **Evaporation of Liquids.** (1). The evaporation of liquids is of frequent occurrence in quantitative analysis and there is perhaps no other operation in which the chances of error are greater. The long time required gives opportunity for contamination by dust from the air and by the solvent action of the solutions on the vessel in which the evaporation is made. There is also danger of mechanical loss due to rapid boiling or to spattering when solids begin to separate.

(2) **Rate of Evaporation.** With the exception of special cases (49, 10) the rate of evaporation may be as rapid as possible

provided there is no mechanical loss. Water solutions can be taken to dryness on the water bath or steam box with no danger of spattering, therefore, when possible, such work should be planned to go on over the noon hour or at night. It is sometimes desirable as a time saving device to heat a solution over a Bunsen burner just short of the boiling point till it becomes concentrated or till one must leave the laboratory, and then set it on the steam box. In carrying out this plan, it must be remembered, that as the volume of liquid becomes less, the tendency for it to boil with a given flame under it, increases.

When the constituent to be determined is but a small percentage of the sample, thus reducing the effect of small losses (35), the solution may be boiled down in a covered vessel. The best way of doing this is to have the liquid in a casserole which is then held in the hand and kept moving over a free flame. With practice, great skill can be acquired in this operation.

(3) Action on Glass. Acid liquids attack glass and porcelain far less than alkalis. The difference is so great that whenever it is permissible, liquids to be evaporated should first be acidified. If the subsequent operations require an alkaline reaction, the slight excess of acid can be neutralized. Common glass is attacked much more than hard glass or Jena glass. Porcelain is more resistant than glass and far less likely to crack on being heated. In refined work platinum vessels must be used.

(4) Protection from Dirt. A watch glass furnishes ample protection but when placed on a beaker or dish in the usual way, convex side down, the rate of evaporation is greatly reduced. To obviate this, a glass triangle should be made by bending a piece of stirring rod into the shape of a V and laying it across the top of the vessel as a support for the watch glass which can then be put on convex side up. This permits a readier escape for the steam and the condensation on the cover does not drop back.

For large dishes a piece of paper or pasteboard supported three or four inches above the top is to be recommended. Paper can be tacked to a light wooden frame or held in concentric wooden hoops which can then be supported in a clamp attached to a ring stand. A pane of glass, if not too heavy, can also be held in a clamp above the dish and makes an ideal cover.

**65. Quantitative Transfer of Liquids.** When, in the course of a quantitative analysis, liquids must be transferred from one vessel to another, the following procedure must be followed: The liquid is first poured out to the last drop, the vessel being held in an inverted position for some seconds to permit drainage from the sides to take place. The lip of the beaker or dish is then touched to the receiving vessel to remove the last drop after which the outside of the lip is rinsed off and the vessel brought to an upright position. The rinsing out of the inside is accomplished by washing down the sides with a stream from the wash bottle. This should be carried around the extreme top so that the whole surface is reached. The minimum quantity of water is used and the rinsings added to the receiving vessel as described above. This rinsing is repeated two or three times. The points to observe are, contact of the whole interior surface with the rinsing water, the use of the smallest possible quantity of water each time, and the careful drainage before adding fresh water.

Occasionally the solution after its transfer, is to be diluted further, in which case care need not be taken to keep down the volume. When extreme care is to be used on this point, the rinsing is accomplished by using small portions of water at a time and causing it to flow over the sides by appropriate turning and inclining of the vessel.

**66. Testing Reagents.** (1). The legend "c. p." on a reagent bottle is so delusive and unreliable that manufacturers have lately begun to give it up and offer instead analyses showing the amounts of the various impurities. This is far more scientific and such reagents from a good firm may safely be used in ordinary work. Contamination may, however, come after the reagent has left the manufacturer. Liquids, especially if alkaline, dissolve material from the vessels containing them and solids receive additions through careless handling. False labels and mistakes in dispensing are possible and the pernicious habit of pouring back into the bottle unused residues, is also responsible for many impurities. All told, the chances of the reagents being sufficiently impure to affect the results, are so great that commercial analytical laboratories regularly test them. The following general method is most frequently employed.

(2) Running a Blank. This simple and effectual plan consists merely in carrying through the whole analysis, however complicated, adding reagents, evaporating to dryness, etc., as the case may be, but leaving out the sample. The appearance of precipitates can then be noted at the various stages. In some cases these should be filtered, ignited and weighed, and the appropriate correction applied to the result of the analysis. (See special case under Determination of Nitrogen, note 4, p. 216.)

(3) Special Tests. It frequently happens that for certain analyses very impure reagents can be used provided the one or at least a few possible substances that might affect the result, are absent. In this case the addition of one reagent frequently will decide the matter. Occasionally a general test for non-volatile material is wanted. To do this, a portion is evaporated to dryness under conditions that insure against introduction of dust from the air and the residue ignited. With volatile solids, a gram or so can be ignited directly.

(4) Distilled Water. This, the most important reagent, is perhaps also the one most frequently contaminated. It should give no non-volatile residue on evaporation to dryness. For most purposes, however, tests can be made with silver nitrate, barium chloride and ammonium oxalate. No cloudiness should be produced with these reagents even after long standing. The tests are best made in flasks which can be stoppered, thus affording sure protection from the fumes of the laboratory.

Ordinary distilled water also, as a rule, contains small amounts of ammonia and carbon dioxide. The latter interferes seriously with certain operations especially in volumetric analysis and can be removed by boiling. (See 110, 4.)

67. **The Care of Platinum.** (1). Mechanical Injury. In the hands of inexperienced students platinum suffers more from mechanical than chemical injury. It is a soft metal and therefore easily dented and scratched. The only remedy is carefulness. Crucibles, dishes and electrodes must be set down gently, must not be allowed to fall and must not be distorted purposely as when a fusion is to be removed from a crucible.

(2) Chemical Injury. Crucibles must not be set low in a gas flame where the hot, unburned gases in the inner cone come into contact with the metal. This produces a gray, crystalline appear-

ance on the surface. Platinum must also not be heated in contact with other metals. Crucibles should be supported in triangles of clay or platinum. A good substitute for a platinum triangle is one of stout nickel wire covered with platinum foil at those points where there is contact with the crucible. Only platinum tipped tongs should be used when holding the crucible in a flame, though hot platinum may be grasped with clean nickel or steel tongs, provided it be removed at once from the source of heat.

The following substances must not be fused or ignited in platinum: Hydroxides of sodium, potassium, lithium and barium, nitrates, cyanides, organic matter containing phosphorus, arsenic and compounds of easily reducible metals such as those of the hydrochloric acid and hydrogen sulphide groups.

The following substances in solution, even at ordinary temperatures, attack platinum: Chlorine, bromine, iodine, ferric chloride and mixtures of hydrochloric and nitric acids.

(3) Cleaning Platinum. Ordinary grease and dirt can be removed by heating in hydrochloric or nitric acid (never the two together.) When this fails to remove stains, sodium carbonate, acid potassium sulphate or borax may be melted in the crucible. Only the low flame of a Bunsen burner should be used to keep the acid sulphate in the fused state. It sometimes requires more than an hour's contact with the melted flux to remove persistent stains. After being cleaned the surface should be burnished with sea sand, that is, a washed sand with round grains. This can be rubbed on wet with the fingers and burnishes the metal without wearing it away. The gray, crystalline appearance which comes after prolonged heating over a gas flame should be removed in this way.

#### *Management of the Laboratory Work.*

68. **The Point of View.** The actual laboratory work in a beginning course in quantitative analysis is illustrative of the science and art of chemical measurements, and unless the student keeps this point in mind and consciously thinks of the general application of what he is doing, he will become a mere follower of directions, unable to proceed if a situation arises which the book does not describe. This applies not only to the purely chemical principles, but equally as much to the manipulation; for it is a

mistake to suppose that the practical work of the laboratory is not capable of classification and study. In Practice I, for example, where the water of crystallization in barium chloride is determined, some thought should be given to the various methods of heating substances to a high temperature without mechanical loss. The actual laboratory work affords practice with at least one such method.

69. **How to Use the Book.** The right attitude of mind can be cultivated by proper methods of using the directions for the laboratory work. The usual habit of working with the book open on the desk and making constant reference to it, as though the matter on the page were being copied, is pernicious in the extreme. The correct way to use the laboratory book is to read through the whole process in order to get the proper perspective, and when ready to begin the actual work, the first step in the analysis should be taken up separately and mastered. The necessary laboratory operations for this first division of the work are then to be carried through without further reference to the book. In a similar manner the next step is studied, the laboratory work done, and so on to the end. For example, the first work in any analysis is the weighing of the sample which should be studied and note made of special points, if any, such as grinding in an agate mortar, certain methods of weighing called for by the nature of the sample, etc., and then, with the book closed and laid aside, the sample is to be weighed. In like manner the method of getting the sample into solution is to be learned and carried out without the book.

70. **Planning the Work.** (1). Constant attention should also be given to the economic management of the laboratory work. Two or more analyses should be started at once, since the time required is but little longer than that for one alone. Extra care, however, is needed in the note keeping and the labeling of the apparatus in order to preserve the identity of each analysis. The simplest plan is to mark every vessel employed in the course of the same analysis with the same number, which is then entered in the note book together with its description. For example, suppose two samples of limestone No. 412 were weighed and their analyses carried on side by side. The identification marks in the note book could be 412 (1) and 412 (2). The small beakers in which the samples are dissolved would be marked 1 and 2. The

first filtrates would be received in casseroles 1 and 2 and the insoluble residues would be in filters 1 and 2, and so on through the whole analysis.

(2). Chances of blundering will be reduced by acquiring the habit when at work of always placing the apparatus in the same relative order on the desk. The easiest order to remember and follow is the natural one of reading from left to right. According to this, beakers, etc., are set in the order 1, 2, 3,—or a, b, c,—according to the system of marking. This order should be preserved even when the marks themselves are not closely related as, for example, 6, 10, 25,—. Whenever transfers are to be made from one vessel to another the receiving vessels should first be set in a row in front of the others and the correctness of their positions checked before and after the transfer.

(3). When evaporationes are to be made or when precipitates must stand a number of hours before filtration, the work should be managed so that these operations can go on over night or, generally speaking, while the student is not in the laboratory. There should also be no idle minutes during the working periods. If the determinations in hand do not demand attention the next practice should be read and preparations made for it; apparatus can be cleaned and repaired; crucibles can be weighed preparatory to the next ignition; or any one of a dozen other things attended to.

**71. Marking Apparatus.** Filter papers, after being folded, should be marked with a lead pencil so it will be visible in the funnel. Porcelain crucibles are unglazed on the bottom thus permitting a pencil mark. Such a mark will last through several ignitions but will be obliterated by washing. Platinum crucibles obtained from the store room usually have a number stamped on them. Casseroles, porcelain dishes and glass vessels of all sorts are easiest marked with a pencil especially made for writing on glass, a so-called glass pencil. Next easiest of application is the gummed paper label. These will last through several washings if the old mark be erased and the new one written before each washing, that is, while the label is dry. Ground glass parts can be written upon with a pencil. Permanent marks made by etching should not be used on borrowed apparatus.

**72. Approximate Measurements.** In the measurements of reagents and volumes of liquid in which solution is made, an error of from 5 to 10 per cent. is usually permissible, that is, if the directions call for dissolving a sample in 150 cc. of water, either 140 cc. or 160 cc. will do as well. Obviously then, much time can be wasted by attempting an accuracy that will serve no useful end. On the other hand, carelessness can never be tolerated and the student should at once practice with measured amounts of water in beakers and flasks till he is able to estimate the larger volumes. For reagents in solution the cylindrical graduate is usually employed. When solids are to be measured roughly, the proper amount is first weighed approximately (34) and its bulk in the spoon spatula then noted. The best rule, is to measure the first time and in the subsequent work, estimate the amounts.

One of the most important points in quantitative laboratory work is to know when to spend time in accurate measurements and when to save time by approximate measurements. Conscious thought must be given to each case as it arises and a decision formed. In doubtful cases a rapid calculation should be made as suggested in 78.

#### **The Quantitative Laboratory Note Book.**

THE KEEPING OF ACCURATE, CLEAR AND NEAT NOTES IS THE MOST IMPORTANT SCIENTIFIC HABIT A STUDENT CAN FORM.

**73. Requirements of a Good Note Book.** The notes on a quantitative analysis should contain the following: (a) The date of the beginning of the analysis; (b) a descriptive phrase indicating the determination to be made and the nature of the sample; (c) a brief phrase indicating the method employed, if this is not made clear by the nature of the precipitate or volumetric solution used (see g); (d) the number or other identification mark of the sample; (e) the data giving the amount of sample taken; (f) the data giving the amount of substance being determined; (g) the formulas or names of all precipitates weighed, or solutions used in titrating and in the latter case, the values of such solutions; (h) the final percentage result; (i) any notes descriptive of minor accidents that might affect the results.

**74. Test of a Good Note Book.** The test of a good note book is this: Imagine another chemist (let us say the head chemist of the laboratory where the student gets his first job) examining it. If he can tell from an inspection of the book and with no more mental effort than is required for reading the pages before him, exactly what the author of the notes has done; how and when he has done it and find all the data necessary for recalculating the final result, it is a good note book. If, on the other hand, he finds difficulty in deciphering the writing and must puzzle over the meaning of certain of the numerical values and finally, on attempting to recalculate the result, discovers that some of the data are lacking, it is a bad note book.

**75. General Rules and Forms.** (1). **The Note Book.** In commercial laboratories where much work of the same kind is done, special books with appropriate headings printed in are used. For the variety of work in a beginner's course, however, a plain book is best. It should not be cheap and poorly made, for a good book promotes good notes. A medium size not too small is best and it is well to have the pages numbered and ruled one way with pale lines. The detachable leaf form has some advantages but the importance of the original notes is so great that it is perhaps better to use a permanently bound book because it will carry with it greater evidence of not having been tampered with or changed. To avoid unnecessary marring of the first pages, the beginner will do well at first to practice with imaginary crucible weights, etc., on sheets of paper the size of the note page.

(2) **Do not Copy.** Put all original data, such as weight of sample, crucible weights, burette readings, etc., first hand into the note book. On no account should the practice be followed of keeping laboratory notes on scraps of paper and copying them later into the book. In the possible event of not having the note book at hand the data should be entered in the usual way on loose sheets which should then be filed. These original notes may be copied into the regular book, but must be marked as follows: Copied from ..... , original filed in .....

Beginners seldom appreciate fully the importance of this rule against copying. The reason for it is the general one of the relative values of copies and originals. A copy of a page of notes can never be more accurate than the original and from the very fact

that it is copied, it always has in it an additional source of error. In research laboratories where the priority of a discovery may be decided by an entry in a note book, or in law suits involving the results of chemical analysis, a failure to produce the original notes may entail great loss.

(3) Method of Entering Data. (a.) The best method of putting onto the page the data and notes of a series of experiments such as those involved in making a quantitative analysis, is a matter of taste and judgment; and if the student will exercise his taste and judgment in experimenting with different forms, success can not fail to come. The following points will be found helpful:

(b) Phrases descriptive of numerical values such as crucible weights, etc. should be begun well towards the left side, the line then being continued with a row of dashes to the right side where the figures should be placed. Occasionally a shorter line containing a numerical value may be placed in the middle of the line. When note is to be made of some special observation, a marker letter is put at the proper point and the same letter before the note which should be written then as a foot-note. Notes descriptive of accidents that might affect the final result have no standing unless entered into the book at the time of the observation. If made after it is found that the result needs explanation they are open to suspicion.

(c) In the case of crucible weights, weight of crucible plus precipitate, etc., the numbers should be placed at once in position for subtracting. Subtraction may then be made on the page. Other arithmetical work, however, should not be done there but on separate sheets which then can be kept or thrown away at pleasure. If the arithmetical work involved in calculating the final result were all put down, the page would be littered up to no effect. The subtraction alone is tolerated because, since the result must be put down, no extra figures are required and the position of the difference obtained indicates its meaning. The student should remember that if all the data are down the result can be recalculated at any time.

(d) It is an excellent practice, especially at first, to prepare the note page in blank before beginning the analysis. All that is necessary then is to fill in the weights of watch glass, crucible, etc. "Xble" may be used as abbreviation for "Crucible".

## SAMPLE FORM.

Sept. 27, '10.

Determination of Ba in Recrystallized Barium Chloride.	
BaSO <sub>4</sub> precipitated by H <sub>2</sub> SO <sub>4</sub> in presence of excess of HCl.	
Watch Glass + BaCl <sub>2</sub> , 2H <sub>2</sub> O.....	10.6946
Watch Glass .....	<u>10.2418</u>
Sample =	0.4528
Xble + BaSO <sub>4</sub> .....	15.0724(a)
Xble .....	<u>14.6406</u>
BaSO <sub>4</sub> =	0.4318
Ba. =	56.13%

(a) Slight loss due to spattering during ignition. Doubtful if loss is weighable.

(e) When precipitates are to be ignited to constant weight (59,) all of the successive weighings should be put down, care having been taken to leave space for these extra figures. Below is a specimen page from a limestone analysis:

Analysis of Limestone No. 247.	Nov. 1, '10.
Sample = 1.0000 g.	
(1) Det. of SiO <sub>2</sub> . Two evaporation on steam plate.	
After HF Treatment.....	22.4842
	<u>22.5710</u>
	<u>22.5712</u>
Xble + SiO <sub>2</sub> .....	22.5722
Xble .....	<u>22.4835</u>
	0.0875
HF Treatment Residue .....	0.0007
SiO <sub>2</sub> = 8.68%	SiO <sub>2</sub> 0.868

The simple way of recording the rather complicated operations in the determination of the silica should be noted. First, silica is to be ignited to constant weight, therefore the weight of the empty crucible is placed lower than usual, thus giving space for the successive weighings to be entered. This method of beginning at the bottom in recording the results of ignitions to constant weight keeps the column of figures solid. Second, when constant weight has been obtained, the precipitate must be treated with hydrofluoric acid and the weight of the small residue is placed at the top of

the column and marked, "After HF Treatment". The various subtractions by which the weight of the pure silica is reached can now all be made with the greatest convenience. The position of the descriptive phrases, "After HF Treatment" and "Pure Silica", etc., should be towards the left, by which the page is kept open.

(4) No special forms will be given here for note keeping when volumetric methods are employed. When this point is reached the student should give the question of a form for keeping the notes sufficient thought to enable him to work out one of his own.

(5) Finally, in addition to the data of the analysis, the student should form the habit of writing out at once clear and concise descriptions of any phenomenon in the course of the analysis that is not understood. No laboratory manual can describe the appearance of every step and there will therefore be many things to note down and look up on occasion. Even the experienced chemist can scarcely carry through an analysis, however simple, without observing some point of detail worth remembering and therefore worth recording. This sort of note keeping can hardly be overdone and it is recommended as one of the surest steps for making progress in this subject, or it might be added, in any other.

#### **Accuracy of Chemical Analysis.**

**76. Standards and Tests.** (1). The degree of accuracy of a chemical analysis is a function of the purity of the reagents, the material of the vessels employed, the method used, and the care and skill of the analyst. In the determination of the constituents of a pure compound the ultimate standard of accuracy is the so-called theoretical composition based on the atomic weights, which, it must not be forgotten, are themselves determined by refined methods of analysis carried out with the utmost care and skill. In the case of a natural or commercial mixture of no definite chemical composition such a standard does not exist and the only test of the accuracy of a result is its agreement with others by the same or different methods carried out with care and skill. This test of close agreement when limited to the work of one person with one method, is a fictitious one because it in no sense eliminates constant errors. Getting practically the same result a number of times in succession is far more an evidence of

uniformity of work than it is of correctness. This points to a general principle that should be applied wherever possible. The uniformity of work should be broken up as much as is consistent with the method. The best way to do this is to vary the amount of sample taken and consequently the amount of reagents. With all its faults, however, this method of duplicating or checking results, as it is called, is the only test available. Purity of reagents proven by a blank experiment (66, 2) and the necessary care in conducting the analysis are of course assumed.

(2). In the case of complete analysis a further slight test of the general accuracy of the work can be obtained from the summation of all results which, theoretically at least, should be 100%, but owing to the inevitable errors it is never exactly that. If, however, the sum of the percentages of the various constituents differs very much from 100% a gross error would be indicated, though but little information would be afforded as to its location. In mineral analysis, which constitutes the majority of the practices in this and other beginning courses, the summation is likely to be more rather than less than 100%, owing largely to the material dissolved from the vessels.

77. **Agreement of Check Results.** It is the custom among analytical chemists to state the agreement of results in percentages of the whole sample, that is, the differences among the several values, rather than in percentages of the values themselves. For example, if two results, 56.47% and 56.17%, be obtained for barium in barium chloride, the agreement is said to be within 0.30%, that being the difference between the two results; whereas it would be more scientific to state the agreement as being 0.5 + %, meaning that the results differed by a little more than 0.5% of their own values.

The former, conventional method necessitates different standards, depending on the amount of the constituent. For example, an agreement within 0.2 to 0.3% is considered good when the percentage is high, 25% and above. With lower percentages the agreement should be closer, down to 0.05% when 1% or thereabouts of the constituent is present. These figures are for experienced chemists. Beginners may allow themselves larger differences according to the following: When the constituent is 20% or higher the agreement should be 0.3%. With the constituent

from 5 to 20% the agreement should be 0.2% and when below 5% the results should agree within 0.1%. Below 1% the differences should be no greater than 0.01 to 0.03%. However, it must be stated, that much depends on the nature of the method. In some cases closer agreement can be secured while in others the above standards would be severe enough for experienced analysts.

**78. Discussion of Errors.** Reference has already been made to this subject in section 35 where errors in weighing are discussed. This should now be reviewed. The rule given there, namely, to calculate the error to percentage of the constituent sought, is general and will apply to other errors as well as to those of weighing. For example, suppose that a sample containing about 40% of the constituent being determined is dissolved in 150 cc. of water and by accident an amount is spilled which is estimated to be 1 cubic centimeter. The following calculations will at once answer the question as to whether such a loss is negligible or not: 1 cc. in 150 cc. is 1 part in 150 or 0.7%. If 0.7% of the sample is affected, 0.7% of each of its constituents is affected in the same way. If one constituent amounts to 40% it will be reduced 0.7% of 40% or 0.28%, practically as much as the allowable error (77) and therefore too large to be permitted. Constituents, however, amounting to only 4% will be changed only 0.03% which is entirely negligible. Another example can be found in the method of weighing described in 37, 4. Suppose 5 grams of sample were dissolved, diluted in a 200 cc. flask and 50 cc. taken for the analysis, and it was afterwards found that the flask had an error of 0.3 cc. This is 0.3 part in 200 or 0.15 part in 100 which is 0.15%. In the case of a constituent which is present to the extent of 70% the effect will be 0.15% of 70% = 0.1% which is a large error. If, however, the constituent is as low as 7%, the effect will be only 0.01% which is negligible. If an error of 0.3 cc. were made in measuring the 50 cc. portion, the percentage error would be 0.3 in 50 or 0.6 in 100 which is 0.6%; much larger than in the first case.

Calculations of this sort can be made rapidly by the plan as illustrated above and since only an approximate result is wanted, the significant figures should be rounded off whenever possible. Other examples of a similar sort will be given under volumetric analysis.

**79. Calculation of Results.** In calculating and recording numerical values, the student is often careless about the number of decimal places used. Obviously decimals beyond the accuracy of the work should not be recorded. In calculating percentages almost any number of places can be determined with a high degree of accuracy so far as the mere arithmetic may be concerned, but it should be remembered that the weighings are accurate only within 0.2 to 0.3 mg.; the factors used are carried only to the fourth decimal place; and the errors inherent in the methods are still greater than these. It is thus seen that a result like Ba=56.342167% is utter nonsense.

No analytical result called for in a beginning course need be given further than the second decimal place. When the student becomes so skillful that his results with ordinary methods have a meaning in the third place he will by that time have acquired sufficient judgment to know when to report them that far.

**80. Method of Reporting Results.** It seldom happens that the precipitate as weighed is the form of combination in which the report is wanted and it becomes necessary then to calculate from the data at hand the amount of the constituent desired. In a formal course in quantitative analysis a particular form is always designated, but when working independently in commercial work a chemist must frequently give considerable thought to the form of combination in which the report is to be made. The following is offered merely as suggestive: When a complete analysis is made the form of combination for reporting each constituent is the one in which it exists in the mixture, when said form is known. It is rather the exception than the rule, however, when the exact form is known, so the various constituents are calculated to simple combinations such as oxides and common salts of the acid forming elements present, all so selected that the summation will be 100%. For example, in limestone analysis, parts at least of the silica and aluminum are combined with oxygen in the form of a more or less complex silicate. The results, however, are calculated as  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  which may be looked upon as a rearrangement of the more complex substance. Certain procedures on the other hand are merely conventional and have no scientific basis. In the examination of the mineral matter in waters, for example, the sodium is combined with chlorine and in

the event of there being more chlorine than will be taken by the sodium the rest is applied to the potassium. If some still remains it would be calculated as magnesium chloride. In fertilizer analysis custom has settled on  $P_2O_5$  as the method of reporting the content in phosphorus; while in the case of iron and its ores, custom is agreed upon calculating the results in terms of phosphorus itself. The above, it is hoped, is sufficient to indicate to the beginner that when the question arises it will be necessary to refer to the special literature on the subject and see what the conventional methods may be.

## VOLUMETRIC ANALYSIS.

The successive operations of a volumetric analysis are, (1) preparation of the sample; (2) weighing the sample; (3) solution of the sample; and (4) titration. The first three of these are seen to be identical with those of gravimetric analysis, but instead of precipitation, filtration, washing, ignition and weighing of a precipitate, there is the single operation of titration which consists in measuring into the solution of the sample just sufficient dilute solution of some reagent that reacts only with the constituent to be determined. On the basis of the volume of the titrating solution used and its value per cubic centimeter, the amount of the constituent in question can be calculated. This single operation of titration, however, involves a study of the measurement of volume, the preparation of the titrating solutions, and the methods by which the completion of the reaction is recognized. These will be taken up in order, beginning with the measurement of volume.

### Measurement of the Volume of Liquids.<sup>1</sup>

**81. Refinement of Measurement.** The necessary refinement of measurement is attained in all volumetric apparatus by confining the liquid at the point where its level is to be read, in a tube of small cross section as, for example, the neck of a flask or stem of a pipette. A relatively small change in volume is thus easily noted by the rise or fall in the surface of the liquid. The delicacy of the apparatus as a measuring device can in this way be increased to any degree by decreasing the diameter at the points where the readings are taken. This cannot, however, be carried too far or the instrument will become troublesome to use and the refinement of reading will go beyond the degree of accuracy with which the volume is defined. For instance, an attempt to measure successive portions of one liter, each with an accuracy of 0.01 cc., would fail; not because the reading could not be made, but be-

<sup>1</sup>In the following sections on the design and use of volumetric apparatus, the bulletins of the Bureau of Standards, Washington, have been used freely.

cause unavoidable changes in temperature, inequalities in drainage and the like would produce differences greater than 0.01 cc.

The diameters consistent with the required accuracy and definition have been worked out for the different instruments and are given under their descriptions in sections 85, 86, and 87.

**82. Reading the Level of Liquid in a Volumetric Instrument.** The surface of a liquid in a tube of relatively small diameter appears from a point outside and approximately at the same level as a curve with the convex side down. Such a liquid surface is called a meniscus and its lowest point is the one read. It will be found, however, that the reading, that is, the coincidence of the lowest point of the meniscus with a mark on the instrument, is largely a function of the position of the eye of the observer, slightly raising or lowering it causing a rather large change. (The student should make the experiment with a burette.) This source of error is known as parallax and is to be avoided by having the eye always in the same relative position when a reading is made. There are many schemes for accomplishing this, all depending on the use of two vertically moving points whose position relative to each other and to the instrument can be kept constant. One then sights across these points at the meniscus and notes the position on the scale.

Two such schemes will be described here, not as being the best but as being the simplest for beginning students. Their use is confined almost entirely to burettes. (See below.) One is to hold a piece of mirror glass flat against the side of the instrument farthest from the observer and then bring the meniscus into line with the image of the eye. The other plan is to put a paper band around the burette, large enough to slide easily and yet sufficiently tight to remain in any position. The front and back of the upper edge of this band are used as sights for taking the reading.

The graduation marks of flasks and pipettes extend entirely around so that parallax can be avoided by bringing the front and back of the mark into line. Burettes are also sometimes marked in the same way.

A normal meniscus is obtained only when the walls of the instrument are wet a short distance above the liquid.

**83. Drainage.** In the case of all instruments marked to deliver it is evident that the amount of liquid remaining on the in-

terior surface must be constant within the limits of error (88). The amount thus retained is always large and is greater and more irregular the more rapid the rate of outflow. By reducing the rate of outflow a point can be found at which the drainage is constant within the desired limits (88). This has been determined for pipettes and burettes of different sizes and is to be found in sections 86 and 87.

For effect of temperature changes on volumetric measurement see 92, 2.

**84. Necessity of Clean Apparatus.** The test of cleanliness (1) should be applied frequently to volumetric apparatus, for unless liquid flows evenly from the surface, the drainage (83) cannot be constant. Fresh cleaning mixture (2, 3) should be used and if this fails, rubbing with a swab dipped in ground pumice is worth trying. Occasionally a piece will be encountered which will not respond to either treatment owing possibly to some characteristic of the glass itself. This can frequently be remedied by swabbing with dilute hydrofluoric acid — 1 part acid to 30 parts water.

**85. Graduated Flasks.** (1) Design. A flask for accurate measurement should have a somewhat more elongated body and a longer and narrower neck than the ordinary type. The bottom should be slightly re-entrant and the general shape such that drainage can take place from the whole interior surface at the same time. The diameter of the neck where the graduation mark is placed should range from 14 to 20 millimeters in the case of a liter flask, to 6 to 8 millimeters for one of 25 cc. capacity. Were the diameter greater than this the refinement of reading (81) would be impaired and anything less would entail too much trouble in using the instrument. Convenience also demands that the graduation mark should not be too close to either end.

(2) Use. Flasks are as a rule used only as containers. For this purpose the liquid to be measured is poured in till the meniscus coincides with the mark (82), care being taken to allow drainage to take place from the upper part of the neck before the final adjustment is made. Adhering drops can be removed with a piece of filter paper.

If the flask is to be used to deliver the indicated volume, a second mark above the first one must be provided (96), the dif-

ference in volume between the two being the amount of liquid which remains on the sides when it is emptied. In order to secure uniform delivery the following systematic procedure must be followed: When the bulk of the liquid has been poured out, the flask is held for thirty seconds in an inclined position so that all parts can drain equally and the suspended drop then touched to a wet surface — most conveniently the inside of the receiving vessel. It must be included in the amount delivered.

For degree of accuracy, see 88. For calibration, see 96.

**86. Pipettes.** (1) Design. Pipettes are of two kinds, those consisting of a narrow tube with an enlargement in the middle, which are designed to deliver a certain fixed volume; and those consisting of a straight tube with subdivisions like a burette. The former is more generally used and will be discussed in detail.

The suction tube of such a pipette should be at least 13 cm. in length and the delivery tube at least 3 cm. and at most 32 cm. long. The internal diameter of the tubes should range from about 9 millimeters in the case of a 200 cc. pipette to not more than 6 millimeters in the smaller sizes. In no case should it be less than 2 millimeters. The graduation mark on the suction tube should not be too close to either end. The orifice in the delivery tube should be of such size that the free outflow will not last more than one minute for any pipette however large, and not less than 15 seconds if the capacity is 5 cc. or less; 20 seconds if more than 5 cc., but not more than 10 cc.; 30 seconds if more than 10 cc., but not more than 50 cc.; 40 seconds if more than 50 cc., but not more than 100 cc.; and 50 seconds for all sizes above 100 cc. (See 83.)

The contraction of the tip to give the desired outflow is best accomplished by heating the extreme end and, by touching it with a piece of scrap glass, drawing it out smaller than is needed. It can then be enlarged gradually by filing across the end.

(2) Use. The proper management of a pipette, though simple, involves points that beginners frequently fail to learn by themselves; therefore a somewhat detailed description of the procedure will be given. (a) The tip is inserted a minimum distance into the liquid from which a portion is to be measured. This is to prevent the introduction of drops that may flow down from the outside if it is wet a considerable distance. (b) Suction is applied with the mouth till the level of the liquid rises an inch or so above the

graduation mark. The trick in this method of filling consists in placing the tongue on the end of the tube in the mouth in such a way that the pipette can be closed while one is still in the act of exhausting the air, that is, while the liquid is rising in the tube. The flow can be stopped in this way for taking breath without allowing any liquid to run back. Skill in the operation is easily tested by attempting to pipette the clear liquid above a precipitate which has settled. It is possible to withdraw several pipettefuls without disturbing the solid in the bottom. (c) When the pipette is full it is lifted from the vessel containing the liquid before the suction tube is taken from the mouth, the end being kept closed with the tongue. The tip is then covered with the forefinger of the left hand, the other end removed from the mouth and the upper part grasped with the right hand, with the forefinger closing the top. It is now comfortably held ready for adjusting the meniscus (82) to the mark. This is done by holding the instrument so that the graduation mark is on a level with the eye, with the tip touching the wet surface of a beaker or other convenient vessel held in the left hand. Air is admitted at the top by lessening the pressure with the finger and when the meniscus coincides with the mark the flow is stopped and the delivery tube at once placed in the vessel to receive the measured portion. (d) The pipette is emptied by holding it in a vertical position, allowing the liquid to flow out freely till rapid dropping ceases, waiting 15 seconds for drainage (83) and then touching the suspended drop to a wet surface, most conveniently the inside of the receiving vessel which can be inclined for the purpose.

The student should practice filling and emptying a pipette according to the above directions. The method of emptying, section (d), is most important.

For degree of accuracy, see section 88. For calibration, see 94.

87. **Burettes.** (1) Design. Burettes are long tubes of uniform bore graduated in fractional parts of a cubic centimeter. One end is closed with a glass stopcock or with a rubber tube carrying a tapering piece of glass like the nozzle of a wash bottle, the flow of liquid being regulated by a pinchcock. This latter, simple style is called a Mohr burette after its inventor. The glass stopcock is to be preferred in all cases excepting with those solutions like the

caustic alkalis which cause the ground glass parts to stick. With these the Mohr burette is a necessity.

Glass stopcocks should be examined to see that they do not leak, a not infrequent occurrence. Regrinding with emery powder will remedy all but the worst cases. To prevent their sticking when the burette is not in use it should be emptied and rinsed with distilled water. A strip of paper is then inserted between the socket and plug to keep the ground surfaces out of immediate contact. The same rule applies to the glass stoppers of flasks.

If, through carelessness in observing the above precaution the cock or stopper sticks, it can be loosened as a rule by tapping it with a piece of wood. If this fails the parts enclosing the stopper or plug should be warmed by brushing with a flame, care being taken to apply the heat only momentarily at any one point and, by constant rotation, to heat all parts equally. Slow heating in this way, accompanied by tapping, will solve most if not all cases.

In setting up the Mohr burette the rubber tube should be 6 cm. long between the glass parts. A direct experiment must also be made to determine the position in which the pinchcock is tight. This can be done by noting whether there is any change in the level of the liquid in the burette on standing five to ten minutes.

The rate of outflow is an important item (83) and, while it is possible to regulate it with the stopcock, it is better to contract the delivery orifice so that the rate will be correct with the cock open full. With free outflow measured near the middle of the scale the level of the liquid should fall about one centimeter (not cc.) per second. The tip can be contracted as described for pipettes in 86, I.

(2) Use. The burette should be held in a vertical position by means of a clamp attached to a suitable support such as a ring stand. The glass stopcock is lubricated by smearing a narrow ring of vaseline near each end of the plug, care being taken not to get any near the center where it is bored.

The instrument is first filled to a point above the zero mark and the excess then drawn off at the bottom till the meniscus coincides (82) with this mark. The tip below the stopcock must be filled with liquid and the whole length of the apparatus free from air bubbles. The suspended drop on the tip is removed by touching it to a wet glass surface.

Two cases may now arise: (a) A definite volume of liquid is to be delivered. In this case the delivery cock is opened full till the meniscus is one or two small divisions above the desired mark when it should be closed and the final adjustment (82) made more slowly, the suspended drop on the tip being removed by touching it to the wet surface of the interior of the receiving vessel or, if the nature of the experiment permits, with a wet stirring rod which is then put into the measured portion. (b) Liquid is allowed to flow out, as in the case of a titration, till a given reaction is completed, when the delivery cock is closed and the position of the meniscus read (82). In case it falls between two of the smaller divisions its position should be estimated and record made accordingly. For example in a burette graduated in tenths of a cubic centimeter, the hundredths are estimated.

For degree of accuracy, see 88. For calibration, see 95.

**88. Accuracy of Volumetric Measurement.** As was shown in section 81 the refinement of reading can be carried further than the volume changes produced by slight variations in the condition of the liquid. Even without providing against these sources of error, however, the accuracy possible with ordinary apparatus is as great as is consistent with other limitations, for example, the sharpness of the color change in indicators. When an extreme accuracy is desired, the solutions are weighed and not measured by volume.

The required accuracy in any particular analysis can readily be found by the methods described in section 78. The actual errors in measuring with the use of calibrated apparatus need not exceed the following:

Instrument.	Capacity.	Accuracy Attainable.	
		cc.	cc.
Flask to Contain.....	1000		0.2
Flask to Contain.....	50		0.03
Flask to Deliver.....	1000		0.5
Flask to Deliver.....	50		0.05
Pipette .....	50		0.03
Pipette .....	5		0.01
Burette .....	50		0.03
Burette .....	25		0.02

This table gives the data for the common, larger and smaller sizes of the different kinds of apparatus. That for intermediate sizes can be estimated. It must not be inferred that these figures represent the required degree of accuracy, for this, in most cases, permits larger errors than the above. They show merely what can easily be accomplished with the ordinary apparatus at hand.

#### **Calibration of Volumetric Apparatus.**

89. **Necessity for Calibration.** It is possible to obtain, at a relatively high price, volumetric apparatus which is sufficiently accurate for analytical purposes, but the ordinary sort which does not carry a special guaranty is likely to contain errors larger than should be made even by a beginning student. This is due in part to hasty methods in manufacture and in part to lack of uniformity in the units of volume employed (91). *It should be made a rule never to use a burette, flask or pipette for important work unless its correctness as a measuring instrument is assured.*

90. **General Method of Calibrating.** In finding the errors of a volumetric instrument advantage is taken of the fact that weighing is a much more accurate method of measurement than the determination of volume. The quantity of water delivered by a "50 cc." pipette can easily be weighed to the third decimal place, that is, with no greater error than 0.001 g. This would correspond to 0.001 cc., a feat of volume measurement far beyond the ordinary pipette of that size.

Calibration then consists in weighing the water contained in or delivered by the instrument in question, and calculating the true volume from the data obtained (92).

Calibration may also be indirect as when the capacity or delivery of a special instrument capable of more than the ordinary refinement of reading (81) is first determined by weighing, and is then used for testing other instruments. (See 96.)

Mercury is sometimes used as the calibrating liquid and has certain advantages but water, being more like the solutions usually employed, is better.

91. **Unit of Volume.** The true liter is the volume of one kilogram of water at 4° centigrade and the "cubic centimeter" is

the one thousandth part of the liter. This unit is the one adopted by the United States Bureau of Standards and is at present rapidly displacing the Mohr liter described below, though much of the apparatus on the market is still graduated in Mohr units.

The temperature of  $4^{\circ}$  is chosen as that at which unit weight of water shall have unit volume because at that point variations in temperature produce the least change in the volume of water. The volume change per kilogram per degree at room temperature, for example, is about 0.2 cc. while in the immediate neighborhood of  $4^{\circ}$  it is less than 0.01 cc.

The use of this standard, however, in determining the capacity or delivery of volumetric apparatus involves considerable calculation (92), which fact induced Mohr to devise an arbitrary system which would be simpler to handle. Mohr defined the "volumetric liter" as the volume of water at  $17.5^{\circ}$  which counterbalances a brass kilogram weight in air. These conditions of temperature and method of weighing were intended to represent those of actual laboratory experience, thus eliminating all corrections.

The Mohr liter came into general use but unfortunately was not followed exactly, temperatures of 15 and  $15.5^{\circ}$  being employed in many cases. These values are still frequently seen etched on apparatus. This use of different Mohr units together with the employment also of the true liter has caused much confusion. Many chemists, not being well informed as to the various standards, have used in the same analysis different pieces graduated on different systems with the result that volumetric methods have at times been discredited when the fault lay in the failure to calibrate the apparatus.

92. **Calculation of Volume from Weight.** (1) The reproduction of the conditions defining the liter would be difficult with the ordinary equipment of the laboratory and indeed would not be desirable for purposes of calibration. The procedure is always to weigh the quantity of water in question at laboratory temperature and then calculate its volume by correcting for the expansion above  $4^{\circ}$  and for the buoyant effect of the air (26, 4).

(2) The volume changes of water over a considerable range of temperature have been determined with great accuracy and are to be found in tables in many of the larger works on quantitative analysis and physical chemistry, in the chemical dictionaries and in

collections of physical and physical-chemical constants. Reference to such tables will show the volume corresponding to a given weight and temperature. (See table below.) The correction at room temperature is about 0.2 cc. per liter per degree.

(3) The difference in the volume of air displaced by a given weight of water and the brass of the corresponding weights is so great that the true or vacuum weight must always be determined (26, 4). This correction amounts to about a cubic centimeter per liter. (See table below.)

(4) The glass of the vessels also expands and contracts with change of temperature but to a very slight extent, the correction per liter per degree being only about 0.02 cc. It is thus seen that if apparatus is marked correctly at the average laboratory temperature a variation of five or six degrees either way is entirely negligible. Nevertheless in the interests of definiteness and accuracy it is desirable to adopt some temperature at which the glass instruments shall be correct and for this purpose the Bureau of Standards has selected 20°. This must not be confused with 4° at which unit weight of water defines the liter. The reason why 4° is not also adopted as the temperature at which the apparatus shall be correct is because it is too far from the average of the laboratory. If a kilogram of water at 4° were put into a flask and the level of the meniscus marked at that temperature, the flask on being warmed to 20°, or room temperature, would hold over 0.3 cc. more than a liter.

(5) Paragraphs 1 to 4 above show that by reference to a table giving the temperature-volume changes of water, the volume of a given quantity can be found by correcting its apparent weight for buoyancy of the air. It is possible, however, to combine all the corrections, including the one for the expansion of glass, into one table. This has been done by Payne. (J. Anal. and App. Chem. VI, 326.) His table is given below, recalculated to 20° as the standard for glass vessels, in place of 25° which he had assumed as the average of the laboratory.

This table was constructed as follows: The apparent weight of a liter of water when weighed in air with brass weights was found for each degree from 15 to 32°. For temperatures below 20° 0.023 g., the correction per degree for the expansion of glass, was subtracted, and above 20° the same amount was added. In

other words, apparatus marked below  $20^{\circ}$  is purposely made slightly less in capacity so that when warmed to the standard temperature it will be correct, and when marked above  $20^{\circ}$ , is made larger so that on cooling it will contract to the correct capacity.

The column marked "Apparent Weight" therefore answers the question, how much water weighed in air with brass weights shall be put into a liter flask so that the mark determined by the position of the meniscus at the given temperature will indicate 1000 cc. at  $20^{\circ}$ . The apparent weight for other volumes is directly proportional.

Temperature of water.	Apparent weight.	Temperature of water.	Apparent weight.
15°	998.0 g.	24°	996.6 g.
16	997.9	25	996.3
17	997.7	26	996.1
18	997.6	27	995.9
19	997.5	28	995.6
20 Standard	997.3	29	995.4
21	997.1	30	995.1
22	996.9	31	994.9
23	996.8	32	994.5

The use of this table is shown by an example: In testing a 50 cc. pipette, its delivery at  $23^{\circ}$  was found to be 49.90 g., when weighed in the usual manner. Reference to the table shows that at this temperature 50.00 cc. should have an apparent weight of 49.84 g., from which it is evident that the pipette delivers 0.06 g. too much. The delivery of the pipette is therefore 50.06 cc. (See 95, 3 for method of calculation when very small amounts are concerned.)

**93. General Operations.** (1) Cleaning and Drying Apparatus. Sections 1, 2 and 84 should be re-read if necessary. Flasks that are to be calibrated to contain must be dry on the inside. They are cleaned in the usual manner, rinsed and drained of the excess of water. The outside is then cautiously heated by brushing with a Bunsen flame, the steam formed being driven out with a current of air. This can be managed by carrying to the bottom of the flask a glass tube attached to the air supplying the blast lamps.

(2) Weighing Water. In calibrating, the quantity of water in

question need never be weighed closer than one decimal more than the volume measurement is defined. For example, the delivery of a pipette is weighed only to the third decimal place (34) because its accuracy in volume measurement does not extend beyond the second place.

Since evaporation during the time of weighing would usually be less than could be measured volumetrically, unstoppered flasks may be used. If, however, the water must remain in the weighing flasks for some time — a condition that will frequently arise with a crowded balance room — one with a glass stopper should be employed, care being taken not to allow the ground glass parts to become wet. These weighing vessels need not be dry on the inside when they are first weighed.

(3) Determining the Temperature. A thermometer graduated in degrees will serve. The accuracy required in a given case can be found by calculating the error on the basis of the data in the table, 92.5. (See also section 100.) Water to be used in calibration should be at the temperature of the laboratory to reduce to a minimum changes during the progress of the work.

(4) Care in Reading. The calibration of instruments and the standardization of solutions call for the greatest possible care in reading, because these are the fundamental operations on the accuracy of which the measurements of volumetric analysis depend.

**94. Calibration of Pipettes.** It will be assumed in the following procedures that the pipette is unmarked or at least incorrectly marked, and that therefore a new and correct graduation must be found. The manipulative details under such an assumption include the simpler case of merely determining the delivery from the original mark. Before beginning the operations described below, sections 81 to 93 should be read and understood. An appropriate note page (75, 4) should be prepared in blank so that the minimum time need be spent at the balance.

(1) The rate of outflow is first determined and, if necessary, is regulated according to 86, 1. The approximate location of the mark from which the desired volume will be delivered can be found by drawing water into the pipette from a burette. An arbitrary paper scale one or two inches long with lines about  $1/16$  inch apart is then pasted onto the suction tube in such a position that the approximate location of the graduation mark falls about the

middle. Such a scale can easily be made from a strip of gummed label by copying onto it the marks on a burette. It should be about  $1/8$  inch wide.

(2) The pipette is filled to some mark near the middle of the paper scale and the water delivered into a weighed flask. Flask and water are then weighed. The pipette is again filled, this time to the upper mark of the scale and the water allowed to flow out to the lower mark, it being received in the flask containing the first and larger portion to which it adds but a small volume. Flask and water are again weighed. From these data the weight of water delivered from the mark first selected and the weight of water contained in that portion of the stem covered by the scale can be found. This latter amount divided by the number of scale divisions will give the weight corresponding to one division. A reference to the table (92, 5) will show the weight of water at the temperature of the experiment which corresponds to the desired capacity of the pipette. The problem now is to find a mark on the scale from which this amount will be delivered. The delivery from the mark first selected which can be called mark "A" is known. If this is less than the desired amount, its weight is subtracted and the remainder divided by the weight corresponding to one scale division. The result will be the distance above the mark "A" from which the desired amount will be delivered. Fractional parts of the scale can be estimated. An analogous procedure is of course to be followed in case the delivery from mark "A" is more than the desired amount. Having once located the correct mark, it should be verified by making several weighings of the total delivery from it.

The above procedure for locating a mark on a volumetric instrument is general and will apply with slight modification of details to all cases.

(3) Under ordinary circumstances the new and correct mark when once found, would be etched on the pipette. With the practice work of students, however, this is not admissible because the instrument is a borrowed one and ought not to be marked permanently. A temporary mark which will withstand ordinary washing must however be used and can be made as follows: The paper of the scale is carefully scraped off below the new mark so that the location of the mark will be defined by its lower edge. An-

other strip of gummed paper is now cut of sufficient length to reach from the new mark to a point a little below the old one etched on the glass, and wide enough to extend entirely around the tube. (Owing to the drawing out of the tip the old mark will invariably be below the new one.) This second paper is then attached so that its upper edge just coincides with the lower edge of the scale, that is, with the location of the new mark. A short pencil line is then drawn, registering with the old mark on the glass in order to locate the paper so that any displacement can at once be seen. The scale is then scraped away leaving only the paper band, the upper edge of which marks the point from which the desired volume is delivered.

It should be covered with paraffine, a little of which can be melted in the spoon spatula and poured onto the tube which should previously be warmed. After cooling, the excess is scraped from the glass leaving only the paper covered. A marker applied in this way will withstand ordinary usage for months.

If lines registering with the old and new marks be made on a separate piece of paper and this be filed away, a new marker can be made and put on in a minute or so, if by accident the first one is destroyed.

**95. Calibration of Burettes.** The sections on general manipulation, 81 to 93, should be reviewed.

(1) The outflow of the burette is first regulated and attention given to the other points mentioned in 87. It is well also to prepare a note page in blank so the time at the balance will be reduced to a minimum.

(2) The water delivered by the successive intervals 0 to 10 cc., 0 to 20 cc., 0 to 30 cc., and so on to 0 to 50 cc., is weighed and by appropriate subtractions (see below) the weights corresponding to the intervals 0 to 10 cc., 10 to 20 cc.....40 to 50 cc. are found. On the assumption that short sections of the burette are uniform in bore, the value of any 1 cc. section of the scale can be found by dividing the delivery of the interval by 10. Further details of the method of calculation may be obtained from the following example:

Interval of Scale Weighed.	Weight $T = 23^\circ$	Interval	Weight	Volume	Volume of "1 cc."
0 to 10	9.958 g.	0 to 10	9.958 g.	9.990 cc.	0.999 cc.
0 to 20	19.978	10 to 20	10.020	10.052	1.005
0 to 30	29.979	20 to 30	10.001	10.033	1.003

The values of the fourth column are obtained from those of the second by subtracting each number from the one next larger.

(3) The simplest way of calculating the volumes from the weights is to take advantage of the close agreement between the numerical values of the two measurements when applied to water and, in the case of very small amounts, call them equal. For example, the weight of water at  $23^\circ$  delivered by the interval 10 to 20 cc., is 10.020 g. At this temperature (See table 92, 5) 10.00 cc. weigh 9.968 g. The interval in question is evidently too large and delivers 10.02—9.968 or 0.052 g. in excess of the amount as marked on the scale of the burette. This 0.052 g. may at once be called 0.052 cc., thus giving the value 10.052 cc. In all strictness the volume of 10.020 g. water at  $23^\circ$  should be calculated according to the expression  $10.020 : x :: 996.8 : 1000$ .  $x = 10.05216$  cc. The difference is 0.00016 cc., a quantity that must be multiplied by 100 before it falls within the ordinary error of reading the burette.

To obtain the volume corresponding to each cc.-mark, successive multiplications and additions are made as follows:

Burette Reading.	Calculation.	Result.	Final Value.
1 cc.	.....	0.999 cc.	1.00 cc.
2	$0.999 \times 2$	1.998	2.00
3	$0.999 \times 3$	2.997	3.00
4	$0.999 \times 4$	3.996	4.00
5	$0.999 \times 5$	4.995	5.00
6	$0.999 \times 6$	5.994	5.99
7	$0.999 \times 7$	6.993	6.99
8	$0.999 \times 8$	7.992	7.99
9	$0.999 \times 9$	8.991	8.99
10	.....	9.990	9.99

Burette Reading.	Calculation.	Result.	Final Value.
11	$9.99 + 1.005$	10.995	11.00
12	$9.99 + (1.005 \times 2)$	12.000	12.00
13	$9.99 + (1.005 \times 3)$	13.005	13.01
14	$9.99 + (1.005 \times 4)$	14.010	14.01
15	$9.99 + (1.005 \times 5)$	15.015	15.02
	* * *	* * *	* * *
19	$9.99 + (1.005 \times 9)$	19.035	19.04
20	.....	20.042	20.04
21	$20.042 + 1.003$	21.045	21.05
22	$20.042 + (1.003 \times 2)$	22.048	22.05
23	$20.042 + (1.003 \times 3)$	23.051	23.06
	* * *	* * *	* * *
29	$20.042 + (1.003 \times 9)$	29.069	29.07
30	.....	30.075	30.08

In this manner the value for each cc.-mark is found, the results of the various arithmetical operations, being given through three decimals. For the final value, however, these are rounded off to the nearest hundredth.

The complete notes should be tabulated as above and for convenience the final values may be copied onto a strip of paper or card board and tacked up for reference.

The only question remaining is that of the correction for points lying between the cc.-marks, a reading for example, like 21.3 cc. An inspection of the table above shows that the variations in the burette are such that the error may be called constant for short distances, therefore the rule is to apply the correction of the nearest cc.-mark. In the illustration above, 21 cc. on the burette = 21.05 cc.; therefore 21.3 cc. on the burette would be 21.35 cc.

(4) The common method of calibrating a burette by drawing off the successive portions of water in tandem, for example 0 to 10 cc., 10 to 20 cc., 20 to 30 cc., etc., while simpler in manipulation, is incorrect in theory because it does not follow the procedure in titration (87, 2) in which the starting point is zero. Owing to the difference in drainage the two methods do not give the same results and therefore the one which more nearly agrees with the manipulation of titration should be employed.

(5) When many burettes are to be calibrated, a so-called calibrating pipette can be used. An instrument of this sort is de-

scribed in Morse's Exercises in Quantitative Chemistry and also in Am. Chem. J. 16, 479.

Greater accuracy will of course be obtained by using smaller intervals, for example 5 or 2 cc., in the calibrations; and in any event, if a large error is found for a given interval of the scale, it should be investigated by determining several points in it.

**96. Calibration of Flasks.** The general sections 81 to 93 should be reviewed. With the ordinary analytical balances which do not permit of loads greater than 200 g. only the smaller flasks can be calibrated by weighing. The method, however, is fundamental and will be described.

(1) By weighing. (a) If the flask is to contain the desired volume it is dried, counterpoised and additional weights corresponding to the volume of water at the given temperature are put onto the pan. It is then removed and water added through a funnel, so as not to wet the neck, till a trial shows that equilibrium is nearly reached. The final adjustment can be made most conveniently with a small pipette, or by adding a little in excess and then gradually reducing it by touching strips of filter paper to the surface. When within four or five milligrams of equilibrium, the position of the meniscus is noted and marked as described in 94, 3.

The determination of the capacity when filled to a given mark consists merely in finding the weight and temperature of the water contained in the flask and from these data calculating the volume.

(b) If the delivery from a given mark is in question, the flask is filled to said mark, emptied (85, 2) and the water so delivered weighed.

If it is desired to locate a mark from which a given volume will be delivered, the following procedure will be found sufficiently accurate: The flask is first filled and emptied (85, 2) and while still wet is counterpoised and the desired amount of water added as described in (a) above. It will then contain the quantity called for by its delivery plus the amount normally retained after it is emptied. The position of the meniscus can be marked as described in 94, 3.

(2) Volumetrically. Owing to the fact that accurate balances capable of carrying the load of a large flask of water are not always available this method is perhaps the most important. The

plan is simply to measure into the dry flask the requisite amount of water by means of a calibrated pipette. No attention need be given to the temperature of the water excepting to see that it does not change while the measuring is being done, for a vessel once calibrated delivers the volume called for irrespective of ordinary changes in temperature (92, 4). 500 cc. pipettes provided with stopcocks at the lower end and calibrated as described in 94 should be at hand for the larger flasks.

By measuring instead of weighing the water into the wet flask, calibration to deliver (1, b above) can also be done by this method.

### **Standard Solutions.**

**97. Definition and General Methods of Preparation.** (1) The solutions which are employed in volumetric analysis for measuring the amount of constituent to be determined are commonly called standard solutions. In its most general sense, however, a standard solution is one the concentration or value of which per unit volume is known with sufficient accuracy for use in quantitative analysis.

(2) The determination of the concentration or value is called standardization, and may be accomplished (a) by dissolving a weighed amount of substance in a definite volume; (b) by determining gravimetrically the amount of dissolved substance either by precipitating from a measured portion or by evaporating a measured portion to dryness and weighing the residue; and (c) by volumetric comparison with another solution of known value. No general rule can be given, the method to be used in any case being decided by the chemical nature of the substance.

**98. General Points in Procedure and Manipulation.** (1) Strength of the solution. In addition to its adaptation to specific analytical methods, such as factor weights or a system like the normal basis, the strength of a standard solution is also governed by its relation to the limitations of the measuring apparatus and the sharpness of the end point.

(a) If too concentrated, the unavoidable variations in measurement—always amounting to several hundredths of a cubic

centimeter — carry with them a quantity of the dissolved substance greater than the allowable errors of the process. For example, 1 cc. of a hydrochloric acid solution containing 0.0091 g. HCl per cc. will neutralize 0.01 g. NaOH. If one gram of sample be taken, 1 cc. of the acid will indicate 1% of NaOH and 0.1 cc., 0.1%, etc. If, however, the acid solution contained 0.0910 g. HCl per cc., 0.1 cc. of it on the same basis would equal 1% and 0.01 cc., 0.1%. In this case the results of several titrations would vary 0.2 to 0.3% due entirely to the use of the too strong solution.

(b) If on the other hand a standard solution is too weak, a relatively large volume will be required to turn the indicator. Measurements of volume can be made to the nearest drop (about 0.04 cc.), therefore if larger portions must be added to show the end of the reaction, nothing is gained in accuracy and there is the disadvantage of working with the larger volume of solution.

If, however, the solution is not used in titrating but as a standard whereby a given amount of material can be measured, the accuracy is increased by increased dilution because the errors of volume measurement carry with them less of the dissolved substance.

(c) The strength of a standard solution to be used in actual analysis should, if possible, be such that ordinary care in reading the burette — that is, without the use of special contrivances to avoid parallax—will not result in errors greater than the allowable ones of the method. This is in the interest of rapidity of work.

(2) In standardizing solutions, the measured portion, the concentration of which is to be determined, should be of sufficient volume that the errors of measurement are small percentage errors. Example: If the strength of a hydrochloric acid solution is to be determined by precipitating with silver nitrate, and only 1 cc., were used, the error of 0.02 to 0.03 cc. in measuring would be 2 to 3% of the whole amount. If 50 cc. were used, such errors in the determination of the volume would be only 0.04 to 0.06% of the whole.

When the standard of the solution is to be determined by titrating with it a weighed amount of some pure salt or a measured volume of some other solution, the value of which is known, the amount of pure salt or volume of known solution should be such that from 25 to 40 cc. of the solution being standardized will be required. The errors of measurement will thus be small percent-

age errors and the reading will come at a convenient place on the burette.

(3) For the preparation of a solution of a certain exact strength one general rule suffices: It is first made slightly stronger than wanted, its exact strength determined and then diluted to the desired point. The opposite scheme of starting with a too weak solution and adding the calculated amount of substance will not work owing to the difficulties of measuring accurately small amounts of concentrated material.

The details of manipulation involved in quantitative dilution according to the above rule will depend on the volume of solution to be handled and the measuring instruments at hand. Assuming the latter to consist of a liter flask graduated to contain, a 50 cc. pipette and a burette, the following is suggested:

(a) Calculate the volume of strong solution which contains the proper amount of dissolved substance for a liter of the desired strength. If this is less than 500 cc., measure it into a *dry* liter flask with the pipette and burette, and fill to the mark with water. If, however, it is more than 500 cc., the necessary amount of water is first measured into the flask and solution is added to the mark. This plan, it is seen, calls for the direct measurement of the smaller volume.

(b) Calculate the volume of water to add to one liter of the stronger solution to dilute it to the required value. The liter flask, which in this case need not be dry, is rinsed with the strong solution and filled to the mark. It is then emptied into a *dry* bottle of sufficient capacity, the measured amount of water added, and the whole thoroughly mixed. To recover the small amount of strong solution which remains on the walls of the flask, it is rinsed several times with the liquid from the bottle, the rinsings in each case being returned. In this way the flask finally remains wet with the correct, dilute solution the loss of which occasions no error.

A disregard of the original portion on the walls of the flask would not introduce a large error. Students should calculate its effect, assuming it to be 0.5 cc. It can also be eliminated by the use of a flask calibrated to deliver (96).

(4) The proper way to mix a solution is to invert and right the containing vessel at least seven or eight times.

(5) Beginners should make up from 1500 to 2500 cc. of a standard solution. A smaller amount is frequently consumed in its own standardization. The five-pint green glass bottles in which liquid reagents are shipped make excellent containers for students' use.

(6) The general, systematic basis for making solutions is given in section 102.

**99. Preservation of Standard Solutions.** (1) A bottle with a closely fitting, ground glass stopper is the best container for a standard solution. In the case of the caustic alkalis, however, like sodium hydroxide solution, a rubber stopper should be used to avoid cementing of the ground glass parts. If it is to be put away for any length of time a paper should be tied over the neck and stopper as a protection against dust. Such solutions being quite dilute as a rule act very little upon glass. Even caustic alkalis require months before any change in strength can be noticed. The special chemical nature of each solution must, however, be considered. Some decompose on long exposure to the light and must therefore be kept in the dark. Others absorb carbon dioxide or oxygen from the air and must be protected by the interposition of suitable guard tubes.

(2) Especial care must be used in handling standard solutions in order to preserve their integrity. No appreciable evaporation should take place and no water should be added. If a transfer to another bottle must be made it should be dry or be rinsed first with some of the solution in question. This point applies with special emphasis to the use of the regular volumetric apparatus, the flask, burettes and pipettes. Filling a wet burette or pipette with a standard solution is equivalent to diluting the solution before measuring it.

**100. Effect of Temperature Changes on Standard Solutions.** The temperature coefficient of expansion of a solution is not the same as that of the solvent but in the case of the dilute water solutions employed in volumetric analysis, it may be called the same without introducing an appreciable error. The effect on the standard of a solution due to a change in temperature can therefore be calculated from the table in 92, 5. For example, suppose a hydrochloric acid solution to have been standardized at 18° and used subsequently at 25°. Assuming 50 cc. to be the amount

taken, it will be seen that the expansion from 18 to 25° is 0.07 cc. In other words at 25°, 50.07 cc. must be taken to give the same amount of acid or, putting it another way, 50.00 cc. of the acid at 25° is equivalent to 49.93 cc. at 18°.

**101. Statement of the Value of a Standard Solution.** (1) The first and natural suggestion is to give the value in terms of the dissolved substance. For example, the strength of a sulphuric acid solution would be given as so much H<sub>2</sub>SO<sub>4</sub> per cubic centimeter. Since, however, such a solution is used for measuring the amounts of other substances, the point must be emphasized that its value can be calculated in terms of anything with which it reacts directly or indirectly or is in any way equivalent.

(2) If a standard sulphuric acid solution contains 0.0490 g. H<sub>2</sub>SO<sub>4</sub> per cc. its value can also be given in other terms of which the following are examples:

(a) The amount of any substance with which it reacts directly. Examples, 1 cc. = 0.1222 g. BaCl<sub>2</sub>, 2H<sub>2</sub>O; 1 cc. = 0.0691 g. K<sub>2</sub>CO<sub>3</sub>.

(b) The equivalent amount of another acid. Example, 1 cc. = 0.0365 g. HCl; 1 cc. = 0.0631 g. HNO<sub>3</sub>.

(c) The amount of any term of a reaction in which it could be concerned. Examples, 1 cc. = 0.1167 g. BaSO<sub>4</sub>; 1 cc. = 0.0220 g. CO<sub>2</sub>.

(d) The amount of any substance with which it can be related through a series of equations. Example, 1 cc. = 0.0974 g. Pt. An ammonia solution could be titrated with the standard sulphuric acid and then, by way of comparison, the ammonia could be determined by precipitating with chlorplatinic acid and igniting the resulting (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub> leaving behind the platinum which is then weighed. An inspection of the stoichiometrical relations will show the following: H<sub>2</sub>SO<sub>4</sub> = 2NH<sub>4</sub>OH = (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub> = Pt from which the amount of platinum equivalent to 0.0490 g. H<sub>2</sub>SO<sub>4</sub> is found by solving the expression, H<sub>2</sub>SO<sub>4</sub> : Pt :: 0.0490 : x. x = 0.0974 g. Pt.

(3) From the above it is seen that the value of a solution can be stated directly in terms of the constituent being determined. The calculation, therefore, of the amount of constituent when determined by volumetric analysis need consist of nothing more than multiplying the value of 1 cc. by the volume of solution used.

(4) Calculation is entirely eliminated from the individual analyses by the use of factor weights (37, 6). Such an amount of sample is taken that the volume of the solution employed in the titration will give directly the percentage of the constituent sought. According to this, 1 cc. = 1%. The sample, being 100%, is therefore one hundred times the value of 1 cc. of the solution. Example: If potassium carbonate is to be titrated with the sulphuric acid above, the factor weight will be  $0.0691 \times 100 = 6.91$  g. Practically, this large amount would not be used, but instead, a simple submultiple of it, like one-half. The burette reading would then be multiplied by 2.

(5) Sometimes a convenient weight of sample is taken and the solution adapted to it. An example of this is the combination, 1 g. sample and a solution, 1 cc. of which equals 0.01 g. of the constituent sought.

(6) For a general, systematic method of stating the values of standard solutions, see 102.

### Normal Solutions.

102. **Theory of the System.** (1) Normal solutions are standard solutions made according to a general system which simplifies the statement of their values and reduces the calculations involved in their use. This is accomplished by making all solutions of such strength that the value of one cubic centimeter is a simple fraction of the molecular weight of the dissolved substance. Since chemical calculations are always based on the molecular weights or simple multiples of them, the labor of finding the equivalent value of such a solution in any desired terms (101, 1 and 2) consists of nothing more than looking up the molecular weight of the desired substance and dividing it by some whole number. This number will depend on the units adopted and on the reaction involved. (See 103, 104 and 105.)

(2) Facility in the use of normal solutions depends largely upon the habit of considering chemical symbols as representing concrete amounts, therefore it may be well to emphasize this at the very beginning. Since in all strictness these symbols represent relative weights, one will not go far astray in cultivating the habit

of thinking of them in terms of grams. Every symbol of an element should be looked upon as meaning the atomic weight in grams of that element and every symbol of a compound should mean its molecular weight in grams. This latter quantity is used so frequently in physical-chemistry that the word mol has been coined to avoid the repetition of such a long phrase. A mol of sulphuric acid for example, means 98.08 g.H2SO4. Further, in a mol of sulphuric acid there are 2.02 g. H, 32.06 g. S, and 64 g. O. No corresponding word meaning atomic weight in grams has come into use.

As soon as the student has accustomed himself to think of these symbols as grams corresponding to the atomic weight or molecular weight he will find it simplicity itself to write out the amount of any substance which is equivalent to or will react with a given amount of some other substance, when said amount is a simple multiple or sub-multiple of the mol of that substance.

This is precisely the fundamental principle of normal solutions. The strength of any solution made on this system is always a simple factor of the mol of the dissolved substance. This means weight in grams and the equivalent weight in grams of any other substance can be found with no more labor than dividing its mol by some whole number.

**103. Neutralization Reactions. Normal Acid and Alkaline Solutions.** (1) Normal solutions in this group are the easiest to understand because their peculiar properties are due to only two constituents, the acid hydrogen of acids and the hydroxyl (OH) of alkalis. The most casual inspection of the formula will show how many mols of each to take so that all will be equivalent or will mutually neutralize each other. All amounts of acids must contain the same weight of acid hydrogen and the alkalis must contain equivalent weights of hydroxyl.

(2) The atomic weight in grams of acid hydrogen (1.008 g. H) and its equivalent of hydroxyl (17.008 g. OH) have been selected as the most convenient standards. These amounts in a liter of solution make the "normal solutions" of acid and alkali respectively.

The amount per liter of any acid for a normal solution is found by dividing its mol by the number of acid hydrogen equivalents it contains. For example, 1 mol HCl,  $1/2$  mol H2SO4, etc.

The amount per liter of any alkali for a normal solution is found by dividing its mol by the number of hydroxyl equivalents it contains. For example, 1 mol KOH,  $\frac{1}{2}$  mol Ca(OH)<sub>2</sub>, etc.

(3) When the salt of a weak acid hydrolyzes or reacts with water producing an alkaline solution, the ultimate amount of hydroxyl formed that can be neutralized by an acid is the same as if all the metal were in the form of hydroxide. For example, Na<sub>2</sub>CO<sub>3</sub> gives 2 NaOH. The normal solution of Na<sub>2</sub>CO<sub>3</sub> is therefore  $\frac{1}{2}$  mol per liter.

A similar hydrolysis takes place with salts of the weak base ammonium giving rise to acid solutions but they are never employed in volumetric analysis.

**104. Oxidation-Reduction Reactions. Normal oxidizing and Reducing Solutions.** There is so much misconception regarding the nature of oxidation and reduction that a few general statements and definitions will be given before the question of normal solutions of this type will be taken up.

(1) First, the prevalent idea that oxidation and reduction are necessarily connected with oxygen should be dropped. The definition so frequently given, that oxidation is taking up oxygen and reduction is losing it, is only partly true. These are merely examples under a broader classification which includes many reactions in which oxygen is not even indirectly concerned.

(2) Oxidation and reduction always occur together and in exactly equivalent amounts, just as in neutralization, equivalent amounts of acid and alkali react. If, in a given reaction some substance has been oxidized, an exactly equivalent amount of reduction has also taken place. Reactions of this type should therefore receive the name oxidation-reduction instead of oxidation and reduction.

(3) The general characteristic of oxidation-reduction reactions is change of valence. If any element or group has a different valence on one side of a chemical equation than on the other, the reaction belongs to this class. The separate processes of oxidation and reduction are determined by the character of the element or group undergoing the change, that is, whether it is positive or negative, and the direction of the change, that is, whether the numerical value of the valence has decreased or increased.

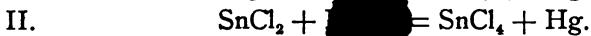
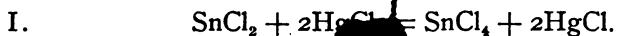
(4) Oxidation is an increase in the valence of a positive element or group, or a decrease in the valence of a negative element or group.

Reduction is the converse; a decrease in the valence of positive elements or groups, or an increase in the valence of negative elements or groups.

Free elements have zero valence.

Oxidation-reduction differs from neutralization in the fact that change in valence is not confined to any pair of elements or groups such as the H and OH of acids and alkalis, but is a process that may be undergone by many elements and groups. There is also the further difference that the degree of change may be different among the several elements, that is, the numerical value of the valence change may vary even in the case of the same element when different reactions are concerned.

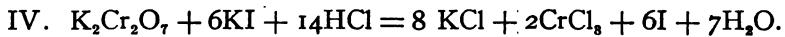
(5) The following typical reactions will illustrate the above points:



In reactions I. and II. the tin changes in valence from 2 to 4. In reaction I., the mercury changes from 2 to 1, and it is to be noted that the change of 2 on the part of one atomic weight in grams of tin is just equal to the change of 1 each on the part of the two of mercury. In reaction II. both the tin and the mercury change the same number of valences. Both elements are positive; therefore, according to the definition the tin is oxidized and the mercury reduced.



Here the negative group  $\text{Fe}(\text{CN})_6$  has been oxidized from a valence of 4 to that of 3. The negative chlorine has been reduced from 0 to 1.



In IV. the two positive chromiuns have been reduced from valences of 6 to valences of 3, a total change of 6. The negative iodine has been oxidized from 1 to 0. Six iodines changing 1 each, balance two chromiuns changing 3 each.

When permanganate of potassium acts as an oxidizing agent in acid solution the valence change of the Mn is from 7 in  $\text{KMnO}_4$  to 2 in the manganous salt formed. If, however, its reduction takes place in neutral solution, the valence changes from 7 to 4 only.

(6) The measure of oxidizing-reducing action, it is seen from the above, takes into account not only the number of mols or atomic weights in grams which undergo the change in valence, but also the extent of the change. It is in short the product of the two. For example, in reaction IV, the oxidizing effect of a mol of dichromate of potassium is determined by multiplying the number of chromiums by the valence change of the chromium, that is,  $2 \times 3 = 6$ . Similarly the reducing effect of a mol of stannous chloride (reactions I. and II.) is seen to be 2. Obviously if a mol of dichromate has an oxidizing power of 6 and a mol of stannous chloride a reducing power of 2,  $1/6$  mol of  $\text{K}_2\text{Cr}_2\text{O}_7$  will react with  $1/2$  mol  $\text{SnCl}_2$ , and if the manganese in potassium permanganate (5) above changes in valence from 7 to 2 when it acts in acid solution, the measure of the oxidizing effect of a mol is 5.  $1/5$  mol  $\text{KMnO}_4$ , therefore, is equivalent to  $1/6$  mol  $\text{K}_2\text{Cr}_2\text{O}_7$ .

(7). On the basis of the points developed in (6) above a suitable standard for oxidizing and reducing solutions can be obtained. It is the mol divided by the product obtained by multiplying the number of atomic weights in grams of the element undergoing the valence change by the numerical value of the change. It is equivalent to an atomic weight in grams of an element changing 1 in valence, and may be called the oxidation-reduction unit<sup>1</sup>.

A normal oxidizing or reducing solution may now be defined as one which contains one oxidation-reduction unit in a liter. The proper amount per liter of any substance can be obtained by dividing its mol by the number of atomic weights in grams of the element which changes in valence, multiplied by the numerical value of the change.

The particular reaction which takes place in the method employed must be considered. For example, when potassium per-

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<sup>1</sup>The above method of defining normal oxidizing and reducing solutions is substantially the same as that given by Abegg in his *Anleitung zur Berechnung volumetrischer Analysen*. The author, however, had worked out the scheme and used it in place of the cumbersome "available oxygen" method several years before Abegg's little pamphlet came into his hands.

manganate acts in acid solution the valence change of the manganese is 5, therefore the normal solution is  $\frac{1}{5}$  mol  $\text{KMnO}_4$  per liter. In neutral solutions, on the other hand, the manganese is reduced only to  $\text{MnO}_2$  in which compound it has a valence of 4. The change is then from 7 to 4, or 3, and the normal solution contains  $\frac{1}{3}$  mol per liter.

When elements are used, as is the case in iodine solutions, the atomic weight in grams is divided by the valence change.

**105. Precipitation Reactions. Normal Solutions for Precipitation Methods.** A few volumetric methods are based on the fact that certain precipitations are complete with a very slight excess of the precipitating reagent and that the presence of the excess can be shown by means of a color change in some added substance. For example, if a solution of potassium sulphocyanate,  $\text{KCNS}$ , be added in small portions at a time to a nitric acid solution of silver containing some ferric iron salt, the sulphocyanate will react with the silver forming the precipitate  $\text{AgCNS}$ , till all the silver is precipitated, when the next drop will react with the ferric salt producing the well known deep red color so often used as a "test" for iron. If the value of the  $\text{KCNS}$  solution in terms of silver is known, the amount of that substance is readily calculated.

The precipitation of a mol of a univalent element or group is the unit for normal solutions. The amount per liter for a normal solution of any substance to be used as a precipitating solution is found by dividing its mol by the number of mols or atomic weights in grams which it will precipitate, multiplied by the valence of the element or group precipitated. For example, 1 mol of  $\text{KCNS}$  per liter makes a normal solution because it precipitates one atomic weight in grams of univalent silver. In the volumetric determination of zinc a more complicated situation exists since here 2 mols of  $\text{K}_4\text{Fe}(\text{CN})_6$  precipitate 1 mol of  $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ , that is, 3 atomic weights in grams of bivalent zinc. The calculation is therefore as follows:

$$\frac{2 \text{ } \text{K}_4 \text{ Fe}(\text{CN})_6}{3 \times 2} = \frac{\text{K}_4 \text{ Fe}(\text{CN})_6}{3}$$

One-third of a mol of  $\text{K}_4\text{Fe}(\text{CN})_6$  is the amount per liter for a normal solution.

106. **Nomenclature.** Solutions of full normal strength are seldom employed on account of their being too concentrated for most analytical work (98, 1). To obviate this and still retain the advantages of the system, more dilute solutions are made on the basis of dividing full normal strength by some whole number as 2, 4, 10, etc. Such solutions are indicated by the expressions,  $N/2$ ,  $N/4$ ,  $N/10$ , etc., which are read, half-normal, fourth-normal, tenth-normal, etc. This merely introduces another simple factor into the calculation. For example,  $N/4 \text{ Na}_2\text{CO}_3 = \text{mol Na}_2\text{CO}_3 \div (2 \times 4)$ .

The above method of expressing dilutions less than full normal is the common one seen in practically all text-books.

Another method of indicating the concentration is to write N as the symbol for normal and precede it with the proper factor in the form of a decimal fraction, for example,  $0.5N$  = half-normal;  $0.1N$  = tenth-normal. This method is employed in Chemical Analysis. It is a more elastic plan than the other and will be used in [redacted] book.

A rational procedure is to make all solutions of the normal system on a decimal scale, the very dilute ones being multiples of hundredth-normal and the more concentrated ones multiples of tenth-normal. The series will run  $0.01N$ ,  $0.02N$ ,  $0.03N$  - - -  $0.09N$ . Then, beginning with  $0.1N$ , will go on,  $0.2N$ ,  $0.3N$ , - - -  $0.9N$ . In such a series a solution can be found that in point of concentration will exactly meet the requirements in hand and yet preserve all the advantages in calculation that come from the use of simple numbers.

Under this plan the amount per liter for full normal strength is always multiplied by the decimal to obtain the value of the dilute solution.

107. **How to Calculate with Normal Solutions.** (1) Two things must be learned thoroughly: The reasoning by which the amount per cubic centimeter for a normal solution of any substance is found, and the fact of the equivalence of volume among normal solutions.

The first is to be acquired by practice. As a study plan, lists of six or seven acids, alkalis, oxidizing and reducing agents should be made and the amounts per cubic centimeter for normal solu-

tions worked out. The second point should not merely be learned, it should become a habit of mind, to associate the symbol for normal with the idea of equivalence of volume. For example, 1 cc. of any N-acid reacts with 1 cc. of any N-alkali and is equivalent to 1 cc. of any N-acid. Similarly, oxidizing and reducing solutions are equivalent, volume for volume.

(2) Problems in volumetric analysis take two forms: (a) Having given the volume of standard solution, find the amount of substance with which it reacts or is in any way equivalent (101). (b) Having given the amount of some substance, find the volume of standard solution that will react with it or is in any way equivalent to it (101).

(3) If the standard solutions are on the normal basis, these problems are easily understood and solved by the following reasoning: All normal solutions are equivalent, volume for volume, therefore, if the volume of a solution is given as in (a), the amount of any substance equivalent to it is the amount of said substance in the same volume of normal solution of that substance. If an amount of substance is given, the volume of any normal solution that will react with it or is equivalent to it, will be the same as the volume of normal solution that can be made from the given amount of said substance.

Examples: (a) To what amount of potassium carbonate is 30 cc. of 0.3N HCl equivalent? It is equivalent to the weight of potassium carbonate in 30 cc. of 0.3N  $K_2CO_3$  or

$$\frac{138.30 \text{ (mol } K_2CO_3\text{)} \times 0.3}{2 \times 1000} \times 30 = 0.6224 \text{ g.}$$

(b) To what volume of 0.3N HCl is 0.4704 g. of  $Na_2CO_3$  equivalent? It is equivalent to the volume of 0.3N  $Na_2CO_3$  that could be made from 0.4704 g.  $Na_2CO_3$ , which is found as follows:

$$0.4704 \div \frac{106.10 \text{ (mol } Na_2CO_3\text{)} \times 0.3}{2 \times 1000} = 29.55 \text{ cc.}$$

(4) When insoluble substances or even combinations incapable of existence in the free state are to be considered, their normal solutions are imagined. For purposes of calculation an imaginary solution is as good as a real one. For example, what weight of calcium carbonate is equivalent to 30 cc. of 0.5N HCl?

The answer is, the weight of  $\text{CaCO}_3$  in 30 cc. of an imaginary 0.5 N solution of  $\text{CaCO}_3$ , or

$$\frac{100.13 \text{ (mol CaCO}_3) \times 0.5}{2 \times 1000} \times 30 = 0.7510 \text{ g.}$$

(5) It may be profitable to compare the above calculations with similar ones when advantage is not taken of the normal basis of the solutions. Example (a) would then read as follows: To what amount of potassium carbonate is 30 cc. hydrochloric acid solution equivalent, if the solution contains 0.01094 g. HCl per cc.? The expression, Mol. Wt.  $\text{K}_2\text{CO}_3$  (138.30) : 2 × Mol. Wt. HCl (72.92) : : x : 0.01094, is first solved and the value of x multiplied by 30. This may be put into the same form as given in (a) above and then becomes:

$$\frac{138.3 \text{ (K}_2\text{CO}_3) \times 0.01094}{2 \times 36.46 \text{ (HCl)}} \times 30 = 0.6224 \text{ g.}$$

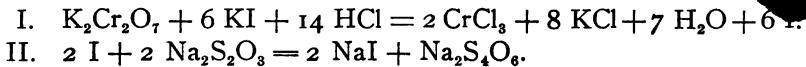
The multiplication by 30 is common to both, therefore the remaining parts of the two formulas should be compared. In the second, two molecular weights must be looked up as against one in the first. The value 138.30 is common to both but in the second it must be multiplied by 0.01094 as compared with the simple number 0.3 in the first. The factor 2 is common to both but dividing by 1000 is much easier than by 36.46.

(6) It is seen that no small part of the advantage of normal solutions lies in their being made so that their values can be expressed by a simple fraction as 0.3N and 0.5N in the examples above. To make the solutions of a certain exact strength (98, 3), however, requires time and trouble that may exceed that of the more complex calculations. There is nevertheless considerable advantage in retaining the normal system even in such cases. A solution can be made of a strength appropriate to the work in hand (98, 1) and its exact value calculated in terms of normal. For example, suppose the value of a hydrochloric acid solution is found by precipitation with silver nitrate to be 0.01136 g. HCl per cubic centimeter. This is calculated to normal by dividing by the amount of HCl in 1 cc. of 1N or 0.03646 g. The result carried to the nearest significant figure in the fourth place is 0.3116. The strength of the acid is therefore 0.3116 N. A value

such as this substituted in examples (a) or (b) above is obviously not so convenient as the simpler one of 0.3N but it is still better than the solution given in (6) in which no use is made of the normal basis.

The real advantage, however, lies not so much in the greater ease of computation, as in preserving the simplicity of the reasoning by which the solution is accomplished. The methods given in (3) above are in no wise changed.

An example from one of the laboratory practices to follow will serve to illustrate the point. A sodium thiosulphate solution is usually standardized by titrating with it the iodine liberated from potassium iodide by a measured amount of a potassium dichromate solution. The reactions are as follows:



Suppose that in an actual experiment 25 cc. of dichromate solution were added to an excess of potassium iodide and the iodine set free required for its titration 23.7 cc. of thiosulphate solution. Required, the strength of the thiosulphate.

If the strength of the standard dichromate is known in terms of  $\text{K}_2\text{Cr}_2\text{O}_7$  per cubic centimeter, the problem is rather long and not readily understood by beginners. If, on the other hand, the value of the dichromate is given on the normal basis, even though it is not a simple fraction of normal, the solution is shorter and easier to comprehend.

Suppose the dichromate to be 0.1135 N. The thiosulphate is then  $\frac{25}{23.7}$  0.1135 N. This can be seen clearly by considering the

three possible cases: First, the thiosulphate is the same strength as the dichromate, that is, 0.1135 N. In this case 25 cc. would be required to react with the iodine. Second, the thiosulphate is stronger than the dichromate, that is, more than 0.1135 N. In this case less than 25 cc. would be required, because the solution being stronger, 1 cc. will react with more iodine than if it were 0.1135 N. Third, the thiosulphate is weaker than the dichromate, that is, less than 0.1135 N. In this case more than 25 cc. will be used in titrating the iodine. The quantitative relation of the normality of the thiosulphate to that of the dichromate is inversely as the

volumes of solution used. Students should not attempt to remember a formula in a case of this sort, but rather the reasoning by which the relation is established.

(7) Factor Weights with Normal Solutions. In 101, 4 the general method of factor weights with standard solutions is given. The same rule applies to those on the normal basis. The sample for analysis should be 100 times the value of 1 cc. of the solution. One cubic centimeter then equals 1% and the number of cubic centimeters used gives the total percentage.

When the standard solutions are normal the calculations are simple. One has but to write down the amount of the constituent to be determined that would be required for 1 cc. of a solution of [redacted] same normality as that used in titrating. One hundred times this is the factor weight.

Examples: (a) What factor weight of iron ore is to be used with 0.1N  $K_2Cr_2O_7$  solution? The answer is, 100 times the weight of iron in 1 cc. of 0.1N solution of iron. Iron changes 1 in valence, from  $Fe^{''}$  to  $Fe^{'''}$ , in the reaction with  $K_2Cr_2O_7$ , therefore the atomic weight in grams, 55.99, is the amount for a liter of normal solution. In 1 cc. of 0.1N there is 0.005599 g. This is 1% of the sample to be taken which, when multiplied by 100, gives the whole sample, 0.5599 g.

(b) What factor weight of sample of oxalic acid,  $H_2C_2O_4 \cdot 2H_2O$ , should be used with 0.2186N alkali? The mol of oxalic acid is 126.05 and it contains two equivalents of acid hydrogen. The factor weight is therefore

$$\frac{126.05 \times 0.2186}{2 \times 1000} \times 100 = 1.3777 \text{ g.}$$

### Indicators.

**108. Definition.** An indicator is a substance used in volumetric analysis to show the point at which sufficient standard solution has been added to react with the constituent being determined. The familiar litmus is an example. If dilute acid be added slowly to an alkaline solution containing some litmus, the blue color remains until all of the alkali is neutralized, when there is a sharp change to red, thus indicating the point at which the re-

action is complete. The indicators employed in neutralization reactions (103) constitute a special group and will be considered in section 110. Those used in oxidation-reduction (104) and precipitation (105) reactions have but little in common and must be considered individually.

109. **End-Point.** (1) The change in color at the completion of the reaction is called the end-point, the quality of the indicator being determined by the sharpness and distinctness of the change produced by the addition of a drop more or less of the standard solution. (See also 114.) The nature of the color change differs according to the indicator. In practically all oxidation-reduction and precipitation reactions it consists in the formation of a highly colored compound between the indicator and the first slight excess of the titrating solution after the main reaction is complete, or the reverse of this; the disappearance of a colored compound of the indicator and substance being titrated when the latter is completely transformed by the standard solution. In the case of indicators used in neutralization reactions the nature of the color change is more obscure.<sup>1</sup>

In all cases, however, whatever may be the nature of the color change, the cause lies in a change in the concentration of the constituents of the main reaction and the indicators may be looked upon as qualitative reagents for one or both of these constituents. The characteristic reaction is given when the concentration reaches a certain value which it may approach from either side. For example, in the titration of iodine with thiosulphate (p. 179) the blue color of the starch-iodine compound disappears when the concentration of the iodine is reduced below a certain value. In the reverse titration in which a standard solution of iodine is employed, the blue color appears as soon as a faint excess of iodine is added beyond that required by the substance being titrated. In a similar manner the indicators employed with acids and alkalis may be considered reagents for acid hydrogen and hydroxyl. (For a more complete discussion of this special case, see 110.)

The sharpness or distinctness of the end-point, irrespective of

<sup>1</sup> The nature of the color change in indicators of this group will not be discussed in this work. For an account of the older or Ostwald theory any text-book of physical chemistry can be consulted. The modern or Stieglitz theory is to be found in the J. Am. Chem. Soc. 25, 1117.

the nature of the indicator, is affected by various conditions chief among which are the following:

(2) Concentration of the Standard Solution. The more concentrated the standard solution, the sharper will be the end-point. The existence of an end-point or sharp change in color depends upon a discontinuous or step-wise change in the concentration of the main constituents of the reaction, since otherwise the color change would not be discontinuous but gradual, one shade slowly merging into the other. This step-wise change in concentration is brought about by adding the standard solution drop by drop near the completion of the reaction, the successive steps being measured by the amount of active reagent in a drop or, in other words, by the concentration of the solution. By diminishing the concentration of the standard solution, the amount of reagent in a drop can be made so small that the drop-wise addition amounts, in effect, to a gradual change in concentration. For example, in titrating an alkali with 1N acid, one drop of the acid will produce a sharp change in color. On diluting the solution to 0.1N and in other respects preserving the same conditions of the experiment, it will be found that special methods (113, 4) may have to be used to determine a color change with one drop more or less. If the solution then be diluted to 0.001N and added drop by drop, the change in color will still take place but will require several cubic centimeters to produce it, and, which should be especially noted, will be gradual making it impossible to determine at any one point between these extremes just when the alkali was neutralized.

The dependence of the sharpness of the end-point on the step-wise change in concentration of the main constituents of the reaction is general for all indicators and sets the limits to which the dilution of the standard solutions can be carried. When the end-point becomes indistinct with a drop more or less, nothing further can be gained in the accuracy of the measurement by increasing the dilution. (See 98, 1).

(3) Volume of Solution Being Titrated. The change in concentration produced by the addition of a drop of standard solution is also a function of the volume of liquid to which it is added. A drop of 1N acid in a liter of solution is the same as a drop of 0.1N acid in 100 cc. Therefore sharpness of end-point is pro-

moted by keeping the volume of solution to be titrated as low as is consistent with other conditions of the experiment.

(4) Concentration of the Indicator. This is an important point which students are likely to leave out of consideration. For every indicator there is a certain concentration which gives the sharpest end-point under the conditions in hand. No general rule can be given. An experienced chemist can judge by the depth of color produced and the beginner must acquire experience by experimenting. (See 113, 2.)

(5) Among other conditions affecting the sharpness of the end-point may be mentioned, (a) the nature of the indicator. Some are more delicate than others and respond to smaller changes in the concentration of the main constituents of the reaction. (b) The direction which the change in reaction may take, as for example, whether acid be titrated with alkali or an alkali with acid. This difference is usually small. (c) The presence of other substances. (d) The temperature. (e) The color of the light in which the end-point is to be observed. Of this latter point it may be said that with few exceptions diffused daylight is the best light.

(6) In the case of bi-colored indicators an intermediate shade can as a rule be observed between the two main colors and it becomes a question as to which color change to select as the end-point, that from the first main color to the middle shade or that from the middle shade to the second main color. Generally there is little difference in distinctness, the important point being to use the same end-point in analysis as in standardization (114). In any event a simple experiment will determine the best end-point for any special case (113, 2).

110. Indicators for Use with Acids and Alkalies. (1) This large group can be discussed together because in reality they indicate the completion of but one reaction, that between acid hydrogen and hydroxyl, the essential constituents of all acids and alkalies. (Compare with oxidizing and reducing agents, 104 4.)

As qualitative reagents (109, 1) these indicators may be divided into two groups, one more sensitive to acid hydrogen than to hydroxyl and the other, the reverse, more sensitive to hydroxyl than to hydrogen. Phenolphthalein (111, 3) is an example of

the first and methyl orange (111, 2) of the second. The difference in sensitiveness of these two groups is sufficient to cause them to give opposite reactions in neutral (110, 5) or nearly neutral solutions and to render one or the other of them entirely worthless under certain conditions (110, 2, c). To enable a proper selection of indicator to be made in a given titration, and to understand its peculiar behavior when not adapted to the case in hand, the various conditions affecting the concentrations of hydrogen and hydroxyl must be reviewed.

(2) Concentration of H and OH in Solutions. (a) Since H and OH are the characteristic constituents of acids and alkalies, their general reaction may be written,  $H + OH \rightleftharpoons H_2O$ , the double arrow indicating that the reaction is reversible, that is, that water, the product of the reaction, dissociates in its liquid form to give a small amount of H and OH, or, from another point of view, that the reaction does not go completely to an end, some of the original constituents remaining uncombined. In the reaction between equivalent amounts of acid and base the quantity of H and OH left uncombined is infinitesimally small when considered in connection with ordinary quantitative analysis. At room temperature it is, in round numbers, one ten-millionth mol per liter, or 0.0001 milligram hydrogen and 0.0017 mg. hydroxyl.

If either acid or base is in excess, its mass action effect (45, 2) causes more of the other constituent to go into combination, thus diminishing its concentration. The considerations in section 43 will apply here and it may be stated that as the concentration of the one (H or OH) increases, that of the other decreases in the same ratio with the result that in any solution the following equation holds true: Conc. H  $\times$  Conc. OH = Constant. If, for example, the concentration of H in water or in the solution resulting from the mixing of equivalent amounts of a strong acid and a strong base, be doubled, that of the hydroxyl will be halved and the amount per liter will then be 0.0002 mg. H and 0.00085 mg. OH. If an indicator is sufficiently sensitive to hydroxyl it will show the alkaline color in such a solution in spite of the excess of acid hydrogen present. This is actually true of methyl orange.

(b) The degree of ionization in the case of very weak acids and bases may be so small as to reduce the concentration of the hydrogen and hydroxyl to such a point that certain indicators will

no longer be affected, for it is the actual concentration at a given moment that is shown by an indicator and not the potential or possible amount that can be titrated. This difference is important and every effort should be made to understand it. For example, a solution of carbonic acid made by passing carbon dioxide into water will require for its neutralization a considerable amount of alkali, yet the ionization of the  $H_2CO_3$  is so small that the concentration of active hydrogen is only a small fraction of one per cent. of the total. The result is, that indicators like methyl orange do not give the distinct acid color in the presence of carbonic acid alone. The red, alkaline color of phenolphthalein, on the other hand, is at once discharged.

The difference between the actual and potential concentration of acid hydrogen is also shown by the more familiar acetic acid. In 0.1N solution this acid is only 1.4% ionized. In other words, the actual concentration of H in such a solution is really 1.4% of 0.1N or 0.0014 N. According to Salm<sup>1</sup> this is the limit of the sensitiveness of methyl orange towards acid hydrogen and, as experiment readily shows, this indicator in 0.1N acetic acid gives a color strongly tending towards the alkaline yellow. In comparison with 0.1N HCl which is 90% ionized, the difference in color of methyl orange in the two solutions is marked.

(c) Hydrolysis also affects the amount of hydrogen and hydroxyl in solutions of the salts of weak acids or bases and in the sense that salts of weak acids such as carbonic, hydrosulphuric, boracic, hydrocyanic, acetic and in general most organic acids, give alkaline solutions and those of the weak bases like ammonium give acid solutions. The actual concentration of H and OH in such solutions varies inversely as the degree of ionization of the acid or base from which the salt is derived. Sodium carbonate, for example, being the salt of the very weak carbonic acid (see b above), gives solutions in which the concentration of hydroxyl is so high that considerable acid must be added before the red color of phenolphthalein is discharged. Acetic acid on the other hand is moderately strong and its salts accordingly give only slightly alkaline solutions in which the concentration of hydroxyl is not sufficient to redden phenolphthalein but will change the color of methyl orange. The hydrolysis of ammonium salts is of the same

<sup>1</sup> Z. physik Chem. 57, 471.

order as that of the acetates, ammonium hydroxide being ionized to about the same extent as acetic acid. The concentration of hydrogen is sufficient to discharge the red color of phenolphthalein but does not affect that of methyl orange.

From the above considerations it is seen that hydrolysis will play an important role in titrations involving either a weak acid or a weak base. The concentrations of hydrogen and hydroxyl will be conditioned not only by the amount of titrating solution added, but also by the hydrolysis of the resulting salt, thus causing the end-point to take place without definite relation to the strength of the standard solution and that of the liquid being titrated. Five combinations are possible:

- I. Titration of a weak base by a strong acid.
- II. Titration of a strong acid by a weak base.
- III. Titration of a weak acid by a strong base.
- IV. Titration of a strong base by a weak acid.
- V. Titration of a weak acid (or base) by a weak base (or acid).

In I. and II. the same salt will be formed and being from a weak base, it will give an acid solution. With an indicator like phenolphthalein that is very sensitive to acids, the end-point in I. will come too soon, that is, before the equivalent amount of strong acid has been added. (See third paragraph below.) In II. it will come too late, that is, the acidity due to the hydrolysis must be counteracted by an extra amount of the base. Such titrations require the use of an indicator like methyl orange that is not very sensitive to acid but highly so to hydroxyl.

In III. and IV. the salt will be the same and coming from a weak acid its solution will be alkaline. With an indicator like methyl orange that is sensitive to hydroxyl the end-point will come too soon in III. and too late in IV. for reasons similar to those given above under I. and II. The proper indicator in these cases is one like phenolphthalein.

Case V. is inserted merely to fill out the series. It is impossible of accomplishment excepting by indirect means. This is, however, a matter of no concern for it need never be tried. The chemist always has choice of the titrating solution and if either weak acid or weak base is to be determined a standard solution

of a strong reagent of the opposite character should be used. Indeed, two of the other cases can also be eliminated by this means. The strong reagent is generally used in the burette so that the titration of a weak base by a strong acid and the titration of a weak acid by a strong base will, in practice, cover all cases. Special reasons, however, may at times call for the reverse procedure.

It might be inferred from the above that in the titration of weak acids or bases, the only objection to an improper selection of indicator is that the end-point comes too soon or too late, that is, does not coincide with the completion of the reaction. Experiment would show, however, that in addition to this fault there is also the other one of lack of sharpness or distinctness in the end-point. The color change is so gradual that it cannot be said to take place at any one point. The cause of this is the same as that described in 109, 1, namely, a gradual change in the concentration of the H and OH. That this must be true can be seen from the reaction of the solutions of salts of the weak acids and bases. If, for example, a solution of ammonium chloride is acid, then in the titration of ammonium hydroxide with hydrochloric acid, two causes determine the rate of increase in the concentration of H: (1) The step-wise addition of the standard solution, and (2) the tendency of the resulting ammonium chloride to form acid hydrogen by its hydrolysis. This tendency increases as the titration proceeds because more ammonium chloride is constantly being formed. The rate of increase in hydrogen due to this hydrolysis is therefore an accelerated one and indeed to such an extent as to counteract the step-wise mode of adding the standard acid. The net result is that the concentration of acid increases gradually and consequently the color change in the indicator is gradual and not sharp and distinct.

The titration of strong bases such as KOH, NaOH and Ba(OH)<sub>2</sub> with strong acids like HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> presents no difficulties as the resulting salts do not hydrolyze.

The student should keep clearly in mind that it is the salts of the weak acids and bases that hydrolyze and not the acids and bases themselves. The following simple experiments will illustrate this point: Phenolphthalein is added to some recently boiled water (110, 4, a) and then a drop of dilute ammonia water. The red color will be produced as readily as by a strong base like NaOH

because there is no salt present and consequently no hydrolysis. The addition of some dry ammonium chloride will, however, at once discharge the red color because of the acid hydrogen produced by its hydrolysis. Similar experiments can be made with methyl orange and acetic acid.

(3) Titration of Polybasic Acids and Their Salts. (a) The behavior of certain acids with more than one hydrogen equivalent in the mol is peculiar, owing to the fact that the different hydrogens ionize in widely different degrees. The dissociation of such acids is always step-wise and in the sense that the first hydrogen is ionized more than the second and the second more than the third, and so on. If now, the difference in the degree of ionization coincides with the difference in the sensitiveness to acid of two indicators, it will be possible to titrate the two separately since the first will give an end-point with the indicator of lesser sensitiveness and the second with the indicator of greater sensitiveness. This is actually true of phosphoric acid,  $H_3PO_4$ . The first hydrogen is sufficiently ionized to give the acid color to methyl orange. So small a percentage of the second, however, is in the active state that methyl orange retains its alkaline color. It is sufficient though, to give the acid reaction with phenolphthalein. The dissociation of the third hydrogen, on the other hand, is so slight that it cannot be titrated with an alkali.

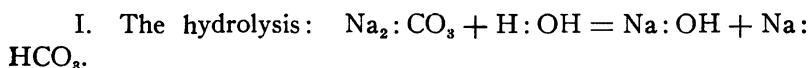
The first of the two hydrogens of carbonic acid,  $H_2CO_3$ , can also be titrated with the use of phenolphthalein.

Students must not make the mistake of generalizing on the above examples. It is not true of all tri-basic acids that the first hydrogen can be titrated with methyl orange and the second with phenolphthalein, and in the case of di-basic acids that the first hydrogen responds to phenolphthalein. It is only when the difference in degree of ionization happens to fit the difference in sensitiveness of indicators that such step-wise titrations can be made. Sulphuric and oxalic acids, for example, also exhibit the same step-wise dissociation, but the difference in degree of ionization of the two hydrogens is not so great. The second is sufficiently ionized to give the acid color even with those indicators least sensitive to acid, therefore the two hydrogens cannot be titrated separately. The nature of each acid must be known before an exact method for its titration can be given.

(b) The reactions of solutions of different salts of polybasic acids is also a function of the degree of ionization of the different hydrogens. The term acid salt applied to compounds like  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{NaHSO}_4$ , etc., refers merely to the fact that some of the hydrogen of the original acid remains un-replaced by a metal. It is confusing in that it gives the idea that all such salts give acid solutions. This is by no means true for, owing to hydrolysis, many of them give alkaline solutions. The nomenclature by which these compounds are called primary and secondary salts, according to whether one or two hydrogens are replaced by a metal, is better in that it avoids this confusion.

(c) Owing to the fact that the last hydrogen of acids like phosphoric and carbonic is practically non-ionized, the normal salts of these acids give strongly alkaline solutions through hydrolysis. The case of sodium carbonate occurs so often in volumetric analysis that it will be given in some detail. When dissolved in water it forms to a large extent ionized Na and  $\text{CO}_3^-$ . The  $\text{CO}_3^-$  at once reacts with the trace of hydrogen from the dissociation of the water, forming thereby  $\text{HCO}_3^-$ . More water dissociates to restore the equilibrium and so on till a large amount of hydrogen has combined with the  $\text{CO}_3^-$ . This leaves a correspondingly large amount of OH in the free state which imparts a strongly alkaline reaction to the solution.

The titration of this solution with a standard acid is the reverse of the titration of carbonic acid with a standard alkali. The acid first reacts with the OH, thus disturbing the equilibrium and causing more  $\text{Na}_2\text{CO}_3$  to dissociate and hydrolyze, till all of the  $\text{CO}_3^-$  is in the form of  $\text{NaHCO}_3$ . These steps may be represented by the following equations:



When the OH is neutralized according to II, and another drop of hydrochloric acid is added, the reaction takes place with the  $\text{NaHCO}_3$  resulting in the formation of  $\text{H}_2\text{CO}_3$ . This is sufficiently dissociated to give the acid reaction with phenolphthalein. Hence, it happens that this indicator gives an end-point when the sodium carbonate is half neutralized. With methyl orange, on the other

hand, the end-point comes when the whole of the carbonate is neutralized.

It is thus possible with the use of the two indicators to titrate a mixture of carbonate and bicarbonate and calculate the amount of each. Phenolphthalein is first used, the end-point being given when half the carbonate has reacted. Methyl orange is then added and the total mixture determined. Mixtures of the hydroxide and carbonate or bicarbonate can be determined in a similar way. The phenolphthalein end-point will come when all of the hydroxide and half of the carbonate has reacted.

By boiling a solution and thus expelling the  $\text{CO}_2$  as formed, the titration of the total carbonate can be made with phenolphthalein.

(4) The Special Case of Carbonic Acid. (a) Owing to the fact that carbon dioxide is a constituent of the air and is frequently found in distilled water, carbonic acid is a constant impurity in volumetric solutions. Fortunately, in most cases it does no harm, but in all titrations involving the use of phenolphthalein or other indicators highly sensitive to acids, it introduces a source of error and must be excluded.

It can be expelled from distilled water by boiling for fifteen or twenty minutes; though it should be noted that when vessels of ordinary glass are used an alkaline water is likely to result. It should not give a red color to phenolphthalein. A vessel of Jena glass or of porcelain should be employed, if possible.

(b) The standard alkali to be used in the titration of weak organic acids like acetic must also be free from carbonates since phenolphthalein is used. While it is possible to prepare and preserve carbonate-free solutions of sodium and potassium hydroxide, there is no indication given if by chance some carbon dioxide from the air does enter. It is therefore better to use a solution of barium hydroxide or sodium and barium hydroxides mixed. Any carbonate in such a solution or any carbon dioxide entering from the air is at once precipitated as  $\text{BaCO}_3$ , so that the solution itself is always absolutely free.

The simplest method of preparation is to add an excess of saturated barium hydroxide solution to a solution of sodium hydroxide. Ordinary distilled water can be used. There will be a copious precipitation of barium carbonate which should be al-

lowed to settle when the clear, supernatant liquid can be siphoned off (58). Owing to the rapid absorption of carbon dioxide from the air it will be impossible to prevent a slight cloudiness from appearing during the transfer. This will be greatly reduced, however, if the receiving bottle is first rinsed with boiled distilled water, and if the delivery end of the siphon is carried to the bottom of the bottle.

The clear or slightly cloudy solution obtained in this manner can now be adjusted approximately to the desired strength (98, 3). Only approximate adjustment is possible because the solution should not be poured out of the bottle. Its volume must be estimated and the water for dilution added.

Because of the rapidity with which carbon dioxide is absorbed, such a solution can not be used in the ordinary manner, that is, by filling a burette by pouring. The burette must be permanently attached to or connected with the bottle in a closed circuit so that it can be filled without exposing any of the solution to the air. Guard tubes or washing bottles must also be provided to prevent the introduction of carbon dioxide. Such arrangements are pictured in every large text-book and are usually to be seen in every large laboratory. After a burette has been connected in this manner and the solution has become clear by settling, the final determination of its strength can be made.

(5) Neutrality, Acidity and Alkalinity. The beginner's conception of these reactions, namely, that neutrality is the absence of both H and OH, acidity the presence of H and absence of OH, and alkalinity the converse, presence of OH and absence of H, is incorrect. Neutrality must be defined as the reaction of a solution or liquid in which the concentrations of H and OH when measured in mols are equal. When the concentration of H exceeds that of OH the solution is acid and conversely when the concentration of OH exceeds that of H the reaction is alkaline. Pure water (110, 2) is a perfectly neutral liquid.

Neutrality, acidity and alkalinity cannot always be determined by indicators. Those that are very sensitive to acid, give the acid reaction in neutral and slightly alkaline solutions. Thus phenolphthalein in water and in sodium bi-carbonate solutions is colorless (acid reaction). Indicators, on the other hand, that are very sensitive to hydroxyl show an alkaline reaction in neutral and

faintly acid solutions. Methyl orange, for example, retains its alkaline color in the presence of carbonic acid. One can now understand why slightly different volumes of standard solution are required for a given titration, depending upon the indicator used.

The above indicators, however, are rather at the extremes in respect to sensitiveness to H and OH, and since they are merely representatives of two types (110, 1) each of which contains a large number of indicators, it might be expected that some would be found midway in sensitiveness that would change color practically at the neutral point (110, 2). If bi-colored, such an indicator should show neutrality at the intermediate color stage, that is, half way between the acid and alkaline colors. This is practically the case with lacmoid.<sup>1</sup>

**III. Preparation and Use of Individual Indicators.** (1) Only a few of the common indicators will be described. The list of those that can be used in neutralization reactions (103) is a long one and space will permit the description of only three. Those used in oxidation-reduction (104) have nothing in common but one is nevertheless described here. Since this work contains no example of a volumetric method based on a precipitation reaction (105) no indicator of that class is included.

Indicator solutions of all sorts are most conveniently handled if kept in bottles fitted as described in section 14. For students' use 150 to 200 cc. are sufficient.

(2) Methyl orange. The dry substance is dissolved in water at the rate of about 0.3 g. per liter.

Methyl orange must be used in cold solutions. As an indicator it is characterized by its extreme sensitiveness to hydroxyl (alkaline color, yellow) and relative insensitiveness to acid hydrogen (acid color, pink). It may be used with the strong acids and bases and with the weak base ammonia, and in the presence of its salts. Salts of certain weak acids such as carbonates, sulphides and borates that are decomposed by mineral acids like hydrochloric, can be titrated with the use of methyl orange. (See 110, 3, c.) It can not be employed with organic acids as a rule nor in the presence of nitrites.

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<sup>1</sup> Salm. Z. physik. Chem. 57, 471.

(3) Phenolphthalein. The dry material is dissolved in alcohol at the rate of about 5 g. per liter. Alcohol may have an acid reaction and must therefore be tested. The acidity can sometimes be removed by boiling, and in any event by redistilling from lime.

Phenolphthalein is colorless in acids and red in the presence of alkali. It is more sensitive to acid hydrogen than to hydroxyl and may therefore be used in the titration of the weak organic acids. It can not be used with ammonia and in the presence of its salts. (See also 110, 3 and 4.)

(4) Cochineal. About a gram of the dry "bugs" is ground fine in a mortar and digested in 100 to 150 cc. of cold, dilute alcohol—one part by volume alcohol and three parts water—for 20 to 30 minutes. The solution is then filtered and is ready for use. See (3) above regarding acid alcohol. Cochineal resembles methyl orange in being more sensitive to hydroxyl than to acid hydrogen. It is especially useful in titrations with ammonia. Salts of copper, iron and aluminum must be removed. The color change is from yellowish red in acids to purple in alkalies and has the advantage that the end-point can be seen readily in artificial light.

(5) Starch Paste. It is well to prepare about 500 cc. of this. Two or three grams of starch are first rubbed to a smooth paste with a little cold water which is then added in small portions at a time to 400 to 500 cc. of boiling water into which it should be thoroughly stirred. The boiling is continued for several minutes when the beaker or dish is removed from the heat and the contents diluted if necessary to about 600 cc. after which 5 g. (roughly weighed) of crystallized zinc chloride<sup>1</sup> are added. The liquid is stirred till the zinc salt has dissolved when it is set aside to cool and settle after which the clear supernatant solution is poured off into a bottle for use. It keeps indefinitely owing to the preservative action of the zinc chloride.

Starch paste is used in reactions involving free iodine with which it gives an intense blue color. When prepared as described above about 2 cc. should be used for a titration.

The presence of a certain amount of iodide is necessary for

<sup>1</sup> Lord's Notes on Metallurgical Analysis, p. 103.

the sharpest end-point. Cold solutions are also better than hot. (See Standardization of Thiosulphate Solution, page 176.)

For another example of an indicator for use with oxidation-reduction solutions see page 170.

*Titration.*

**112. General.** Titration is the art of measuring the amount of a substance by means of a standard solution. It may be accomplished directly by adding standard solution to the solution of the sample till the color change of the indicator shows the completion of the reaction; or indirectly by adding all at once an excess of the standard solution and then titrating the excess by means of another standard solution. This gives a certain amount of control over the nature of the reactions producing the end-point and permits some titrations that would be impossible by the direct method. For example, an insoluble substance like calcium carbonate could not be titrated directly by an acid, but an excess of standard acid can be added and after the carbonate has dissolved, the acid remaining can be determined by means of an alkaline solution. This gives the data necessary for calculating the amount of the calcium carbonate.

Titration corresponds to the weighing of the final precipitate in a gravimetric analysis and in general quantitative manipulation it ranks second in importance only to the art of weighing.

**113. Practical Points.** (1) In preparing for a titration the student should review sections 81 to 89 and especially section 87 on the design and use of the burette and 84 on the necessity of clean apparatus. In setting up the burette it should be adjusted to such a height that the tip just clears the vessel containing the solution to be titrated. A piece of white paper placed under this vessel will greatly aid in observing the color change at the end-point.

(2) Before undertaking a quantitative titration the end-point should be studied. A little dilute solution opposite in reaction to that of the standard in the burette should be prepared (its value need not be known) and a small amount added to water to make about the same volume of solution eventually to be titrated.

Indicator is then put in and the standard solution added from the burette till the characteristic change in color is observed. A few drops of the dilute solution are again added to restore the original color of the indicator and then more liquid from the burette and so on back and forth till the end-point can be hit within a drop. If the first trials fail, more or less indicator should be used. (See 98, 1 and, if a neutralization reaction, 119.)

This preliminary experimenting to learn the end-point should be made every time a new indicator is used.

(3) When the titration of an unknown amount of substance is to be made, the beginner is often puzzled to know how to avoid on the one hand the tedium of adding a large volume of standard solution drop by drop, and on the other, not to overreach the end-point. The chemist of experience recognizes the approach of the completion of the reaction by various signs. At first the substance being titrated is largely in excess and therefore the standard solution from the burette is neutralized the moment it enters the liquid in the vessel below. Presently, however, as more is added the indicator is seen to undergo a local change in color which disappears on stirring. As the end of the reaction approaches, this disappearance of local change takes place more slowly and flashes of the new color are seen momentarily through the whole solution when it is stirred or shaken.

Only long experience and especially "being in practice" enables one to hit the end-point without much tedious drop-wise addition of the standard solution towards the completion of the reaction. Students will scarcely have time to get this skill with any one titration therefore the following trick of manipulation may be employed: After the addition of the indicator but before beginning the titration, a small amount of the solution to be titrated is poured into a separate vessel and held in reserve. The rest may then be titrated rather rapidly and if the end-point is passed, the original color can be restored by adding a little of the reserve solution. In this way the titration can be finished, care being taken at the end to rinse out the reserve vessel either with water or with the solution when its titration is finished. If the rinsings restore the color of the indicator another drop of standard solution must be added.

In all cases when near the conclusion of a titration, the sides

of the vessel should be rinsed down in order to include any drops that might otherwise escape. When a flask is used the same result is obtained by closing it with a stopper or the ball of the hand and shaking it.

(4) When the standard solution is dilute the end-point is likely to lack sharpness (109, 2) thus rendering it difficult to tell exactly when the color changes. When this is the case a comparison flask or beaker should be made ready. This should be of the same size and shape as that in which the titration is being made and should contain the same volume of liquid and the same amount of indicator. As a rule water serves for this comparison liquid though in some cases it is necessary to have a solution like the one to be titrated. A solution, the titration of which has just been finished, is the ideal one to use after the original color of the indicator has been restored. In any event the indicator in the comparison solution should have the color which it has in the one to be titrated. By comparing the two the change in color at the end of the reaction is more readily detected.

(5) It should be pointed out, however, that while the above plan is of great service it cannot take the place of the skill that comes from ten or fifteen minutes experimental study of an end-point as described above. Finally, the student should not allow himself to be influenced by his desire to have the burette reading agree with previous ones. The end-point always occurs in the solution below the burette, look there for it and let the reading come where it may.

**114. Real Meaning of the End-Point.** (1) Statements made in preceding sections have perhaps been confusing in that the end-point in some places is said to mark the completion of a reaction and in others it is pointed out that different indicators may give end-points with different amounts of standard solution. It is only in the general sense that the indicator marks the completion of the reaction. From the standpoint of exact quantitative work the color change is merely a reproducible point to which both the value of the standard solution and the constituent of the sample under determination are measured. It may or may not coincide with the completion of the reaction as given by the chemical equation. For example, in the titration of a given amount of alkali with a moderately dilute standard acid, about 0.1 cc. more will be

required with methyl orange than with phenolphthalein. (See 110, 5.) This is considerably more than the error of measurement and must therefore be taken into account. The deviation from the point marking the completion of the reaction is not as much as this because it lies between the end-points as given by these indicators (110, 5). In other titrations, notably in certain precipitation reactions, the end-point may be 0.5 cc. — measured in terms of the standard solution — from the stoichiometric relation between the standard and substance being titrated.

(2) The possible errors caused by such discrepancies are eliminated by having the conditions of analysis the same as those of the standardization of the solution. If methyl orange was used in standardizing, it must also be used in the analysis. If another indicator is to be employed the solution should be restandardized with it.

In most cases the difficulty can be avoided by applying a correction, the value of which is found by making a blank titration. A volume of water equal to that of the solution to be titrated is treated with indicator and the amount of standard solution required to change the color is determined. This amount is then subtracted from subsequent burette readings. In certain cases where the end-point is influenced by the presence of other substances, water alone will not serve for the blank experiment. A solution must then be prepared in all respects like the one to be titrated but containing none of the material to be determined.

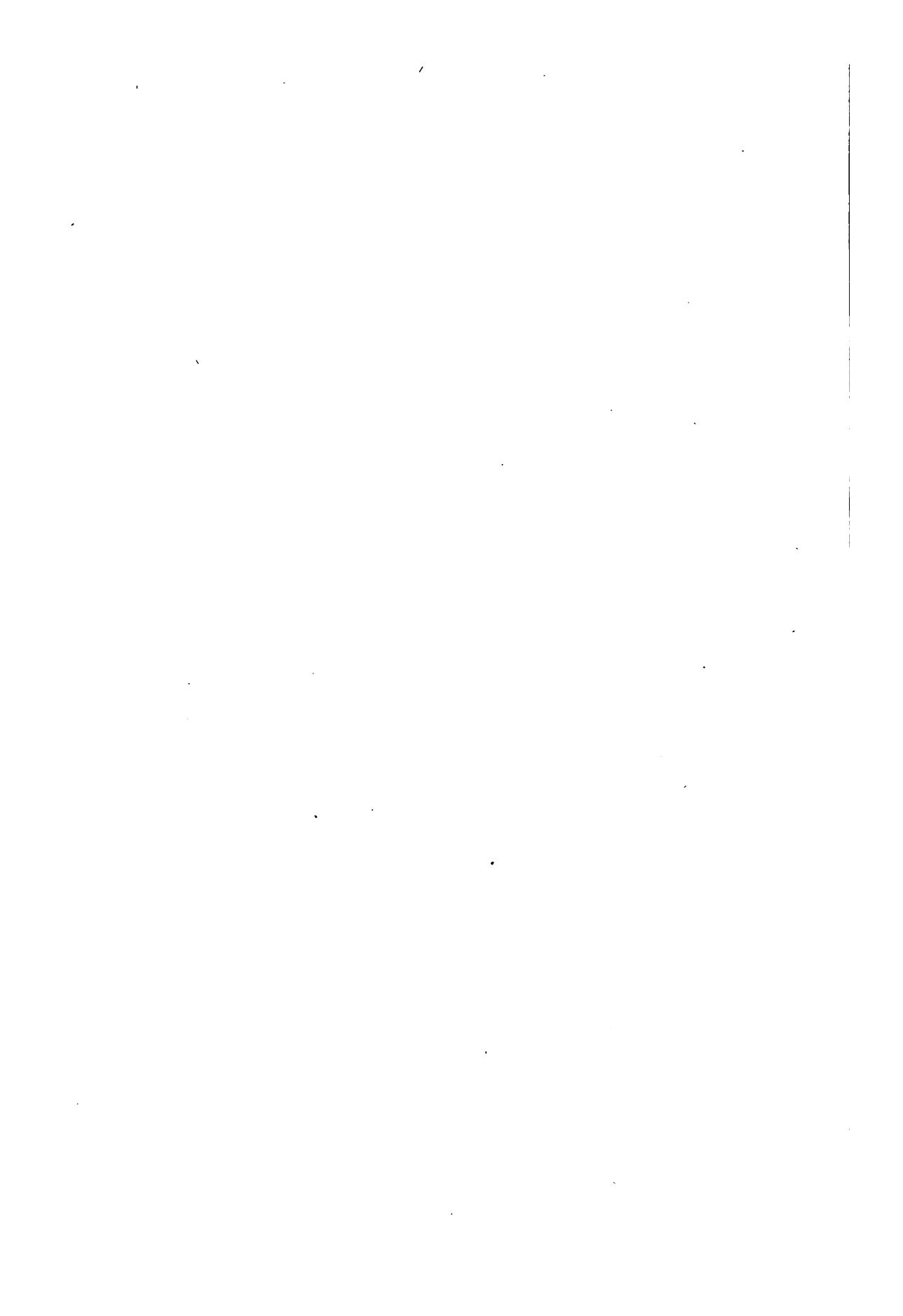
**115. Discussion of Errors and Agreement of Results in Volumetric Analysis.** The discussion of the agreement of check results as given in section 77 applies equally as well to volumetric as to gravimetric analysis. The same can be said of the discussion of errors as given in section 78. Cases arise, however, in volumetric work which do not lead directly to percentage results. For example, in the standardization of a volumetric solution, a series of quantitative results will be obtained regarding which the beginner may well be puzzled to know whether they are in sufficiently close agreement or not. As a case in point, suppose four titrations of sodium carbonate have been made in the standardization of an acid and the results of each titration calculated as follows:

- I. 1 cc. acid solution = 0.008795 g. HCl.
- II. 1 cc. " " = 0.008770 " "
- III. 1 cc. " " = 0.008755 " "
- IV. 1 cc. " " = 0.008760 " "

These values have an unfamiliar look and, though they are apparently in close agreement, the average beginner will be in doubt and will be tempted to ask for help. The puzzle is solved by a modification of the rule given in 78. Instead of calculating the differences to final percentage results, they may be calculated to any terms for which a basis of comparison is known. In volumetric work, the agreement of volume readings is perhaps the most familiar. The table in 88 shows 0.03 cc. to be the average accuracy of a burette. The differences among the values above should therefore be calculated to the effect on the volume of acid required in a titration, for example, where 30 cc. are required. On the basis of 0.008795 g. HCl per cc., 30 cc. = 0.26385 g. HCl. On the basis of 0.008755 g. HCl per cc., 30 cc. = 0.26265 g. The difference is 0.0012 g. HCl. This amount divided by 0.008795, the quantity in 1 cc., gives the volume to which it corresponds, which, on carrying out the calculation, is found to be 0.13 cc. This means that if the same amounts of alkali be titrated, 30 cc. of acid will be required, on the basis of one value, while on the basis of the other value 30.13 cc. (respectively 29.87 cc.) will be used. This is very poor agreement indeed.

A simpler method of calculation is as follows: The difference in the values of 1 cc. is 0.008795 - 0.008755 or 0.00004 g. In 30 cc. this difference would be  $0.00004 \times 30 = 0.0012$  g. Dividing this by the value of 1 cc., in round numbers 0.0088, it is seen to correspond to a volume of over 0.1 cc.

This was, however, the maximum deviation. The next largest difference is 0.000015 g. which corresponds to 0.05 cc. in a titration involving 30 cc. The other differences are still smaller. On the assumption that 0.008795 g. was obtained in the first titration when the student had not yet acquired much skill, it could be rejected and the average of the other three taken as the final value of the acid.



## PART II.

### PRACTICE WORK IN QUANTITATIVE ANALYSIS.

#### A Word to Beginners.

It must not be expected that from the start all results will be satisfactory. If quantitative analysis consisted merely in following directions, it would scarcely pay to give a year or two to the subject. The aim in every determination should be to secure at least *two* good results. A student may reasonably expect this in from three to five trials. If occasionally the first two are correct, it is his good fortune; if in every instance the first two are correct, his instructor will be confronted with the problem of deciding whether he has a great genius in the class or a person to be watched. A series of five or six failures should be no cause for discouragement. It will frequently happen. As a rule two or three determinations should be carried through and if unsuccessful the instructor should be asked for suggestions.

Finally, *the whole or portions of the precipitate and filtrate should be preserved till after the report has been made.* This enables the instructor to make qualitative tests which in many cases will locate the difficulty. It is not necessary to keep all of the filtrate. A portion can be put into a properly marked bottle or even a test tube. A precipitate, after being weighed, can be poured onto a small square of paper and wrapped up. In this way valuable apparatus will not be kept out of commission and the portions so preserved will answer every purpose for a qualitative test.

## I. ANALYSIS OF BARIUM CHLORIDE.<sup>1</sup>

Barium chloride is easily prepared in a high degree of purity and the determination of its various constituents, barium, chlorine and water, is relatively simple and at the same time presents quite a variety of manipulation. These points admirably adapt it for the first practice work.

Its theoretical composition, calculated from the formula  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  is as follows:

$$\begin{aligned}\text{Ba} &= 56.24\% \\ \text{Cl} &= 29.02\% \\ \text{H}_2\text{O} &= 14.74\%\end{aligned}$$

Being a stable, homogeneous material, it can be weighed in an open vessel (37, 1), thus permitting the student to try any of the plans described in 37, 5 and 6. The water is the combined form (38) and while it is given up at a relatively low temperature, the anhydrous salt remaining,  $\text{BaCl}_2$ , may be heated short of redness, which enables the simple method of heating described in 62, b to be used. This involves no special apparatus and is a trick of manipulation for which there is frequent use.

### Determination of Water.

Since, with proper regulation of temperature, water is the only volatile constituent of barium chloride, its determination consists merely in finding the loss in weight on heating. This, to be quantitative, involves the following steps: Weighing an appropriate amount of sample; heating it in a suitable vessel under properly regulated conditions of temperature and without mechanical loss of any non-volatile material; and finally, weighing the residue left from the heating.

<sup>1</sup>The laboratory practice work is given in the order usually followed by the author. The first half of the year is thus devoted to the elements of both gravimetric and volumetric analysis and the second half to more difficult methods selected from both fields. The order may, however, be changed in the latter part of the year, if necessary to adapt it to peculiar laboratory conditions.

Before beginning the actual work section 69 and those on note keeping, especially 75, 2, 3 should be read. It is also urgently recommended that a note page be prepared in blank, allowing space for three weighings in the ignition to constant weight. Several trials should be made if necessary till a neat page is produced.

**Procedure.** (1). Weighing the Sample. The amount should be approximately a gram (40), and while either of the methods described in 37, 5 may be used, the second is recommended; the porcelain crucible in which the ignition is to be made being used as the weighing vessel. Since the material is a pure salt, it is perfectly homogeneous and need not be mixed before weighing (37, 1).

(2) The Ignition. The method described in 60, a, and in another connection in 62, b, should be employed, being careful not to allow the crucible to become red hot and not to heat the salt so rapidly as to cause mechanical loss by a too sudden expulsion of the water. After heating the material in this way for about ten minutes, the crucible is placed in a desiccator to cool (26, 2) after which it is weighed. The heating and weighing are then repeated and so on till constant weight is reached (59, 5).

(3) Weighing the Residue. This presents no special difficulty. Section 30 should, however, be reviewed. The loss in weight is called water, the percentage of which is to be calculated.

**Notes.** 1. In addition to the sections on manipulation to which reference has already been made above, the following should be reviewed: 24, 25 and 35.

2. Calculations similar to those in 35 should be made with regard to this determination in order that the limits of accuracy may be understood.

3. By way of observing the difference between easy and difficult manipulation, the following experiment should be tried: Put a little common salt, sodium chloride, into a crucible and heat it as described above for the barium chloride. Only sufficient time need be spent on this to note the great difference in behavior.

### Determination of Barium.

In addition to the manipulation practiced in the determination of water, that of barium calls for the solution of the sample and precipitation, filtration, washing and ignition of a precipitate. These are the fundamental operations of gravimetric analysis and the ones requiring the greatest exercise of skill and judgment, for in these steps more often than in the weighing, the unskillful manipulation happens which leads to incorrect results. In this connection sections 68 and 69 should be reviewed.

**Procedure.** (1). Weighing the Sample. The factor weight (37.6) for Ba in  $\text{BaSO}_4$  is recommended. Approximately 0.5 g. should be used in any event since more would make too bulky a precipitate. It may be weighed on a watch glass (37.1) and transferred to the beaker (42.1) in which the precipitation is to take place.

(2) Solution of Sample. This is extremely simple since water alone serves the purpose. From 150 cc. to 200 cc. should be used and then 10 cc. (72) hydrochloric acid added (49, 1, 2, 3).

(3) Precipitation. The beaker is covered with a watch glass and set on a wire gauze over a Bunsen burner where the solution is heated to boiling. As soon as this takes place it is removed from the heat, the under side of the watch glass is rinsed off and, by means of a pipette, 10 cc. (72) dilute sulphuric acid—equal parts acid and water—are added in a slow stream with constant stirring, which should be continued for some minutes after the addition of the acid. The beaker is again covered with the watch glass and set aside while preparation is made for the next step.

(4) Filtration and Washing. A funnel, filter and beaker are made ready according to 53, 1, 2, 3. The precipitate may be filtered immediately and is washed with hot water till free from chlorides (57, 1, 2, 3).

(5) Ignition. Either a platinum or porcelain crucible may be used. It should be weighed according to 30. Review 26, 2. Barium sulphate may be ignited together with the filter according to 60, but especial care must be used to allow free access of air. This is accomplished by keeping the crucible on its side and burning off the paper at as low a temperature as possible. After the carbon

is all consumed the full heat of the Bunsen burner should be applied for five minutes when the ignition may be considered finished.

Barium sulphate is perfectly stable in the air, therefore the weighing of the precipitate presents no difficulty. It need not be ignited to constant weight. The percentage of barium is calculated from the amount obtained.

**Notes.** 1. The conditions most favorable to a given precipitation should always receive special study. In the instance above, the excess of hydrochloric acid and the temperature of boiling are factors in causing the precipitate to separate in large particles (49, 1, 2, 3). The effect is indeed so great that the usual precaution of adding the precipitant slowly need not be observed. The mass action of the large excess of sulphuric acid so accelerates the rate of precipitation that the solution may be filtered immediately. Compare these conditions with those for the precipitation of  $\text{SO}_4$  with Ba in excess, p. 143.

2. Barium sulphate when ignited in contact with carbonaceous matter, as the filter, is partially reduced to sulphide with consequent loss of weight, unless the air has ready access to the crucible. If reduction is suspected the precipitate should be moistened with sulphuric acid, cautiously dried, and re-ignited (62, b). This changes the barium sulphide to barium sulphate.

3. The final temperature of ignition for barium sulphate is the full redness of the Bunsen burner. On no account is it to be heated over the blast lamp. This would cause loss of  $\text{SO}_3$  with formation of  $\text{BaO}$ . Suppose this to have been done inadvertently: How could the error be remedied?

#### Determination of Chlorine.

The student will observe that the character of the precipitated silver chloride in this determination is quite different from that of the barium sulphate and will require much more care in its handling. The way the difficulties are met by modifications in the details of manipulation should especially be noted.

**Procedure.** (1). Weighing and Dissolving the Sample. It is recommended that the plan of weighing some simple amount be

followed in this case. 0.4000 g. will be found to give a proper bulk of precipitate. (See Note 1.) This is dissolved in 200 cc. (72) water to which ten to twenty drops of nitric acid have been added. (Note 2.)

(2) Precipitation. Silver nitrate (Note 3) is added to the cold solution in small portions—2 cc. to 3 cc.—at a time, with vigorous stirring after each addition, until the mixture “clears.” This “clearing” is recognized by closely observing the appearance of the liquid. At first, though a heavy precipitate is produced, the solution remains milky throughout. When, however, the point is reached at which the silver nitrate is in excess of the amount theoretically necessary to precipitate the chloride, a change will be noted. The precipitate settles to the bottom and the supernatant liquid, though still very cloudy, becomes noticeably clearer than before. This “clearing” can be taken as evidence of the presence of sufficient silver salt, though a little more does no harm (Note 4). The beaker is now covered with a watch glass, set on a wire gauze and the solution boiled gently for five to ten minutes (Note 5), after which it is ready to filter as soon as the precipitate has settled. Before removing the watch glass the under side should be rinsed off into the beaker.

(3) Filtration and Washing. Silver chloride shows a strong disposition to run through (53,4), therefore a very close grained filter should be used (51). It is washed with hot water till three or four cubic centimeters of the washings on being added to a drop of hydrochloric acid in a test tube, produce no cloudiness.

(4) Ignition. Silver chloride if ignited in contact with the carbonaceous matter of the filter would be reduced largely to metallic silver. On this account the precipitate must be removed as closely as possible from the paper, which is then ignited separately and the ash given a special treatment to transform any reduced silver again to the chloride. (See 61. Method (a) is recommended. The crucible should of course be weighed before beginning the operation.)

The treatment of the ash is as follows: After the crucible has cooled, two or three drops each of nitric and hydrochloric acids are added, the excess of which is then driven off by cautious heating. The main portion of the precipitate is now put into the crucible and, if dark from exposure to the light, it should also be moistened with

a few drops of the mixed acids. The crucible is then set in an upright position and heated as described in 62, b. During the heating the precipitate must be watched closely and if any of the smaller particles in contact with the hottest parts of the crucible show a disposition to melt, the heat is reduced. In this way the material is kept just short of the fusing point for about ten minutes, when the crucible may be cooled and weighed. The heating is then continued till constant weight is reached. The weighing presents no difficulty. From the weight of silver chloride obtained, the percentage of chlorine in the sample must be calculated.

**Notes.** 1. The exact weight of 0.4000 g. is recommended merely to give practice in weighing the sample in this way. Question: What would be the proper factor weight to use, assuming that the sample should be from 0.4 to 0.5 g.?

2. The precipitation of silver chloride is always made in dilute nitric acid solution. This serves the double purpose of promoting its precipitation in good physical condition and preventing the co-precipitation of other substances that might be present in ordinary samples. It is added in the cold to prevent a possible loss of chlorine due to interaction with the chloride.

3. The silver nitrate solution used for precipitation of silver chloride is not the same as that for making the chlorine test (14). Since a change in the appearance of the solution determines the presence of a sufficient amount of the precipitating reagent, the exact strength used is not a matter of importance. A 1-in-20 solution will, however, be found convenient. This expression means one gram in twenty cubic centimeters of the solution. It is made by putting the salt into a graduated cylinder and filling up to the proper mark with water. About 100 cc. of it should be prepared. Any left over can be used subsequently for chlorine testing.

4. The excess of silver solution used when the above directions are followed will be rather larger than would be allowed when the very finest analytical work is attempted. The error introduced by this excess is, however, small in comparison with others inherent in the work and may be neglected.

5. Boiling the mixture after precipitation causes the particles of silver chloride to collect together so there will be less tendency to run through the filter. If the solution stands a number of hours

—over night—in the cold the same effect is produced. Advantage may be taken of this when a precipitation is made late in the afternoon.

6. The whole difficulty of the reducing action of the filter can be obviated by the use of the Gooch crucible (55), but it is good practice to make the ignition as described above, and it is therefore required in this connection.

7. At no time should the precipitated chloride be exposed to direct sunlight as it causes it to blacken with loss of chlorine. Even in diffused daylight a slight darkening takes place, which can, however, be removed by treatment with a few drops of nitric and hydrochloric acids.

**General Notes.** 1. In the study of any analytical method one of the most important questions which the student should ask himself is, *what would interfere, if present?* In the case of gravimetric processes such as the above a general answer would be, everything that is precipitated by the reagents used. For instance a little lead if present with the barium solution would be precipitated by the sulphuric acid. In like manner iodides and bromides would be precipitated by silver nitrate. The student should recall his qualitative analysis at this point and make a list of all bases and acids which, if present, would come down either with the barium sulphate or the silver chloride.

2. Another question also of importance is, what modifications of details in carrying out the analysis are permitted? This does not mean modifications intended to better the descriptions of the notes but changes that may be made under special conditions. For instance, if silver chloride is precipitated late in the afternoon it is better to stir it well and let it stand in the desk over night. The longer time takes the place of the higher temperature of boiling. Likewise, it may happen that after precipitating the barium sulphate there is not time to filter it. Is it safe to let it stand, then becomes the important question. The answer is that it is safe to let it stand and on the following day it may be filtered cold. No notes could give all the contingencies that might arise. The student should, however, think up such situations and ask about them during the lecture hour when the answer can be given to the whole class.

## II. SEPARATION AND DETERMINATION OF IRON AND SULPHUR IN FERROUS SULPHATE MIXTURES.

The samples used in this practice work consist of various mixtures of ferrous sulphate and ferrous ammonium sulphate, in which the iron and sulphur are to be determined. In comparison with the analysis of barium chloride it will be seen that in addition to the determination of these constituents, they are also separated, that is, both are determined in the same weighed sample. New points in manipulation will also be introduced. The samples, being mixtures, have no theoretical chemical composition on which a calculation of the percentage of their constituents can be based. They have been analyzed, however, by the instructor so that the student may know when his results are correct. The method of describing the laboratory work, the procedures, will likewise be changed. Instead of the formal separation into sections according to the different steps involved, it will be given in connected style as is usual in analytical literature. This method will be followed in the subsequent work, excepting where special complexities call for a different form. The student should, however, keep the different steps of the analysis separate in his own mind, always following the study plan as given in 69.

Chemically, the determination of iron and sulphur in such mixtures consists in the oxidation of the iron and its precipitation with ammonia as ferric hydroxide. This is filtered and the  $\text{SO}_4$  in the filtrate precipitated as barium sulphate.

### Determination of Iron.

**Procedure.** Approximately 0.5 g. is the right amount of sample. This may be weighed according to 37,1, not omitting the mixing. Some of the samples, however, are likely to lose water so rapidly that this plan is not feasible, and that of 37, 4 must be used (Note 1). The weighed portion is dissolved in 50 cc. water containing one or two cubic centimeters of hydrochloric acid. In case the method of 37, 4 is used, the acid is added to the portion of

the solution used. A beaker of about 500 cc. capacity is employed to provide for subsequent dilutions. The iron is now oxidized (Note 2) by heating the mixture to boiling and adding nitric acid in cubic centimeter portions till no further action is observed and the liquid has a clear yellowish or amber look. It is then diluted to 200 cc. and ammonium hydroxide added in small portions at a time with intermediate stirring, till an excess is present, which can be recognized by its odor (42, 6, f).

The beaker is then covered with a watch glass and the mixture boiled a few minutes, after which it is set aside to allow the ferric hydroxide to settle, when it may be filtered immediately. This settling is an important item in the case of a gelatinous precipitate. Hot water is used for washing ferric hydroxide, but owing to the adsorption of  $\text{SO}_4$  (Note 3), the first precipitate must be dissolved and reprecipitated and is therefore washed only once or twice after its transfer to the filter. Since solution is to take place in the original beaker, adhering particles need not be rubbed loose.

The solution of the precipitate is accomplished by washing it out of the filter into the beaker in which it was precipitated as described in 42, 5, a. The funnel and filter are set aside, covered, for the second filtration and the mixture of water and precipitate in the beaker is warmed and sufficient nitric acid added to dissolve the hydroxide (Note 4). The solution is diluted to 150 cc. and made ready for the second precipitation by adding a pulped, ashless filter paper prepared by shaking it violently in a flask with about 50 cc. water (Note 5). The volume should now be about 200 cc. The iron is precipitated in the presence of the paper pulp by means of a slight excess of ammonia as described above, and, after settling, is filtered into the original filter and washed with hot water till free from chlorides.

The ignition of the mixed paper and hydroxide may take place in either platinum or porcelain. The moist filter and contents may be put directly into the crucible and dried according to 60, a or b; or the drying can take place more slowly according to 61. The latter plan is perhaps to be preferred, especially if the drying can be arranged to go on over night, since it is extremely difficult to dry the large mass of paper pulp and precipitate rapidly. In any event after the water is all driven out and there is no further danger of spattering, the flame is turned up and the paper is

burned slowly (60). If a platinum crucible is used it may then be heated with the full flame of the Bunsen burner, but with a porcelain crucible in a clay triangle, the ignition should be finished over the blast. A relatively small flame directed obliquely against the bottom and not allowed to envelop the crucible should be used. While over the blast the crucible is kept covered. These precautions are to prevent the introduction of fumes from the flame and consequent reduction at the high temperature to  $\text{Fe}_3\text{O}_4$ . If this is suspected on account of the results being low, the mass may be moistened with nitric acid and reignited.

From the weight of  $\text{Fe}_2\text{O}_3$  obtained the percentage of iron is calculated.

**Notes.** 1. If it is suspected that a given substance gains or loses weight in the air, a gram or so should be counterpoised in a watch glass on the balance as for weighing, and after five minutes another observation made. If there has been a material change in weight, weighing in an open vessel may not be used. To determine just what is allowable, the methods of section 78 should be used. On the basis of the experiment described above, the percentage loss for the time usually occupied in weighing a sample can be estimated and the effect of this loss on the constituents in question then calculated.

If the method of 37, 4 is used, 4 grams should be weighed rapidly, dissolved in water containing a little hydrochloric acid to prevent the precipitation of basic salts, and diluted in a 200 cc. graduated flask. 50 cc. of this solution can then be taken out with a pipette and used for the analysis.

2. The iron must be in the ferric state since the precipitation with ammonia is not complete in the case of ferrous iron. Nitric acid is preferred as the oxidizing agent because no metallic element is introduced by its use. It is necessary to boil the solution to insure complete oxidation. If the precipitate with ammonia is a dirty green in color it shows the presence of ferrous iron and in such an event nitric acid should be added till the precipitate redissolves, when the solution is boiled a few minutes and the iron, now all in the ferric state, again precipitated.

3. The  $\text{SO}_4$  adsorbed by the ferric hydroxide would not interfere with the determination of iron because sulphates of iron

ignite quantitatively to oxide. When, however, the  $\text{SO}_4$  is to be determined it must be taken into account. For a proper understanding of the theory of dissolving and reprecipitating section 48 should be read.

4. Nitric instead of hydrochloric acid is used to dissolve the precipitate preparatory to the second precipitation in order to avoid the introduction of more chlorides. Ferric chloride at a high temperature is volatile, therefore it is absolutely necessary to wash the precipitate till no reaction is given with silver. Ferric nitrate, on the other hand, ignites quantitatively to oxide.

5. The addition of ashless paper pulp is an invention of Dittrich, a German chemist, and is a general scheme applicable to all gelatinous precipitates which are not affected chemically by the carbonaceous matter of the paper. It serves two purposes; hastening filtration and preventing the formation of hard lumps during the ignition. The advantage of the first point is apparent; that of the second appears when the precipitate is to be dissolved after ignition or treated with a reagent. The plan is of special utility in clay analysis where a heavy precipitate of iron and aluminum hydroxides must be dissolved after ignition.

6. The filtrates and washings from the ferric hydroxide precipitates contain the sulphates originally present in the sample and they must be preserved and eventually combined for the determination of the sulphur. The following is suggested regarding a plan of work. On reading the procedure below for the determination of sulphur it will be seen that these filtrates and washings, amounting to 600 to 700 cc. of liquid, must be evaporated to dryness, a very time consuming operation. As soon therefore as the filtrate from the first precipitation is obtained its evaporation should be started. This may be done by setting the beaker containing it over any convenient source of heat—hot plate, steam box, or the like—where it can be kept short of boiling to avoid mechanical loss. Since, however, glass beakers of the cheaper grades are liable to crack under these conditions it is better to filter directly into a porcelain dish or casserole of 500 to 800 cc. capacity. This can then be put onto the hot plate at once. The second filtrate and washings may be received in a beaker and then transferred to the porcelain dish. A slight excess of hydrochloric acid should be added when the evaporation is started. In this connection sections 64 and 65 should be read.

**Determination of Sulphur.**

This determination is the reverse of that of barium and the student should note especially the marked difference in the manipulation required in this case to produce a precipitate of good physical properties.

**Procedure.** The combined filtrates and washings from the ferric hydroxide precipitates above are acidified with hydrochloric acid and evaporated nearly or quite to dryness. (See Note 6 above and also Note 1 below.) The dry or pasty mass consisting of a mixture of ammonium nitrate, chloride and sulphate is then treated with an excess of hydrochloric acid, 15 to 20 cc. or enough to moisten it thoroughly, and again evaporated to dryness on the water bath or steam box. There is sometimes rather violent action after the addition of the excess of hydrochloric acid, therefore the watch glass should remain in position convex side down till all danger of mechanical loss is over. It is then rinsed off into the beaker or evaporating dish and placed on a triangle as described in 64, 4. The residue remaining after the second evaporation is treated with 100 cc. water plus 10 to 20 drops of hydrochloric acid, and if cloudy, it should be filtered (Note 2). The solution is finally diluted to about 300 cc. and heated to boiling when it is removed from the source of heat and barium chloride solution, 1 in 10 (See Note 3, Determination of Chlorine), added—best from a burette—drop by drop with constant stirring (42, 4). About one-half more than is required theoretically should be used. (See 42, 6 and 7.) The stirring is continued for a minute or so after the addition of the barium when the beaker is covered and set aside for at least an hour (Note 3) before filtration. If placed on the steam box or water bath during this time it is all the better, or the solution can stand in the cold over night.

The precipitate is washed with hot water till free from chlorides. In connection with the filtration and washing of barium sulphate when precipitated with barium in excess, section 53, 4 and 57, 2 should be read.

The ignition is performed exactly as described under the Determination of Barium above and from the weight of barium sulphate obtained the percentage of sulphur is calculated.

**Notes.** 1. The evaporation of the filtrate may be carried

on just short of boiling, if found convenient (64), but must be finished at the lower temperature of the water bath or steam box to obviate possible volatilization of ammonium sulphate. The liquid is first evaporated so that the hydrochloric acid added will act in more concentrated solution. Its purpose is to displace nitrates, the presence of which promotes the adsorption of barium from the excess of precipitant used (48). The second evaporation serves to get rid of the excess of hydrochloric acid, which is also undesirable.

2. When a solution is filtered to free it from a precipitate which is to be discarded, the filter must be washed thoroughly and the washings added; the paper may then be thrown away.

3. The student will observe that the physical condition of the product obtained by precipitating  $\text{SO}_4^{2-}$  with Ba is distinctly inferior to that obtained by the reverse process. An excess of hydrochloric acid has a deleterious effect when barium is the precipitant. The solution must stand longer after precipitation. Indeed it is even better if it can stand over night. In the case of a sample containing only a few tenths of one per cent. of sulphur this longer standing would be necessary.

4. The greater detail of manipulation, such as adding the precipitant drop by drop with constant stirring, is all in the interests of producing a precipitate with large particles (49). By way of observing what effect the entire disregard of these directions will have, the following experiment is recommended: Two or three drops of sulphuric acid are stirred into 300 cc. of cold water and precipitated with 25 cc. of barium chloride solution, also added in the cold and poured into the mixture in one portion. Now try to filter it.

**General Notes.** 1. The methods described for the precipitation of the iron and the sulphates are general and apply to all samples in which there are no substances that would interfere. Obviously anything precipitable by ammonia and by barium would have to be removed or another method used. The student should make a list of such substances.

2. The sulphates could be precipitated directly in a separate sample of the salt, but the barium sulphate would be so contaminated with adhering iron that it would be necessary to fuse it and reprecipitate which would consume as much time as the separation of the iron.

### III. ANALYSIS OF LIMESTONE.

Limestone is a rock ranging from an almost pure calcium carbonate to the dolomites or dolomitic limestones containing over forty per cent. of magnesium carbonate. In addition to these main constituents there are also present more or less sand and clay and a long list of minor constituents including sodium, potassium, strontium, titanium, manganese, sulphur, phosphorus, organic matter, and water both hygroscopic and combined. As a rule these minor constituents exist only in traces, with the exception of the combined water, which may reach several per cent. in samples high in clayey matter.

A complete analysis would include the determination of every thing present in weighable amount, but as a rule the requirements for technical purposes do not demand this and only four constituents are determined. The following notes, for example, give methods for silica,  $\text{SiO}_2$ ; iron and aluminum oxides,  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ ; calcium carbonate,  $\text{CaCO}_3$ ; and magnesium carbonate,  $\text{MgCO}_3$ . They are the usual methods for this analysis but are not rigidly accurate because no account is taken of the presence of minor constituents. Some of these entirely escape the precipitations which separate the main elements, while others are thrown down by the same reagents and are therefore included in the determinations given above, making them higher than they should be. (See General Notes, I.)

The calcium and magnesium are calculated as carbonates without actually determining the carbonic acid present. This is also not strictly accurate for in an occasional specimen part of these metals is combined with silicic acid, in which case calculating them as carbonates would be equivalent to calculating into the analysis more than is actually there, with the result that the sum of the constituents would be greater than 100%.

One sample serves for the four determinations, the various separations and precipitations being made successively. This is a common situation in rock analysis in which as many as five or six determinations are often made on one portion. Such analyses require two or three days for their completion and obviously

demand extraordinary care to preserve the quantitative integrity of the solutions through the different precipitations, filtrations and separations.

New points in manipulation are introduced, the most important of which is the sodium carbonate fusion. These new points together with those brought out in the previous practices should now be gone over systematically by reviewing the first 80 sections on principles and manipulation.

#### Solution of the Sample.

**Procedure.** In order to learn the behavior of the material with acids and get a general idea of its character, a pinch should first be treated with cold dilute hydrochloric acid. Violent effervescence indicates a high percentage of calcium and slow, or practically no action, shows high magnesium.

Approximately a gram is the proper amount of sample, which should be weighed according to 37, 1 with due consideration to 37, 5. It is brushed into a small beaker where it is treated with 30 cc. hydrochloric acid — equal parts strong acid and water. This may be added directly or, if the results of the preliminary experiment show that there will be violent effervescence, the plan of 41, 2 must be used. In any event, after the action in the cold is over, the mixture is boiled gently (41, 1) on a wire gauze for five or ten minutes, when the burner is removed, the watch glass rinsed off and laid aside and the solution filtered. (See 53, 4.)

The bulk of the residue is to be noted as it gives an idea of the amount of silica and iron and alumina to expect. A large residue is also likely to consist of clayey matter with the result that the sum of the main constituents will fall considerably short of 100% owing to the combined water in the clay.

The residue is washed with hot water till a drop taken with the stirring rod from the tip of the funnel no longer tastes acid. It is then folded up in the filter and placed moist in a platinum crucible where it is ignited like a precipitate (60) in order to get rid of the paper. The filtrate and washings are set aside in a covered beaker to be added later to the fusion.

The material remaining after the ignition is mixed with about six times its bulk of sodium carbonate and fused according to 41, 4.

The mixing can be done with a stirring rod, any adhering particles being wiped off with a bit of ashless paper which is then put on top of the mixture where it will burn as soon as heat is applied.

When the fusion is completed the cake is transferred to a casserole by one of the methods described in 41, 4. Water is added if necessary, the casserole covered with a watch glass and the acid filtrate from the insoluble residue above poured down the lip in small portions at a time to avoid loss by effervescence (41, 2 and 65). If this solution is not sufficient to neutralize the carbonate, fresh hydrochloric acid must be added. The point of acidity can usually be recognized by the appearance of the yellow color of the ferric chloride coming from the iron in the sample. The liquid, however, will still contain some dissolved carbon dioxide which must be expelled by heating till no more small bubbles are seen to escape. The watch glass is then rinsed off and replaced on a glass triangle, convex side up (64, 4). The entire sample is now in hydrochloric acid solution and ready for the next step in the analysis.

#### Determination of Silica.

**Procedure.** The solution above is evaporated to dryness on the steam box or water bath (Note 1 and 64). The operation can be hastened if towards the end, when salts begin to separate, the crust forming on top be broken up. A stirring rod should be left in the mixture for this purpose. When the residue appears dry it is moistened with 10 to 15 cc. hydrochloric acid which is allowed to act for about a minute when 50 to 75 cc. water are added, the dish again covered with a watch glass, convex side down, and the contents boiled gently for several minutes or, what is as good, digested on the steam box or water bath for half an hour or more. In the latter case it may be filtered immediately; but after boiling the precipitate must be allowed five to ten minutes to settle (49, 9).

In transferring the silicic acid from a porcelain vessel the greatest care must be exercised for, owing to its transparency, it is difficult to see the last traces. The whole inside surface of the casserole must be rubbed hard and an inspection made by holding the vessel at the proper angle to the light to see that every part is

reached. A good plan is to use the finger — assuming it to be reasonably clean — instead of the "policeman." Either hot or cold water may be used for washing the precipitate, cold water being preferable for rinsing off the finger.

The filtrate and washings are returned to the casserole and again evaporated to dryness and the residue treated exactly as described above. A small amount of silica will always be recovered from this second evaporation (Note 1). It should be filtered and washed in a separate filter which may then be placed moist in a platinum crucible together with the one containing the bulk of the precipitate, the paper burned off (60) and the silica finally ignited to constant weight over the blast.

The resulting product, however, is never pure  $\text{SiO}_2$  and must be treated as follows: It is first moistened with a drop or two of dilute sulphuric acid and then rather more than sufficient hydrofluoric acid (Note 2) added to cover it, after which the crucible is set on the steam box or water bath till only a drop or so of sulphuric acid remains. It is then placed in a triangle and the excess of this acid driven off by cautious heating with the burner in the hand, when the temperature may be increased to redness, finally ending with ignition for a few minutes over the blast, after which the crucible is cooled and weighed. The weight of the residue remaining, subtracted from the weight of the original precipitate, gives the weight of the pure silica,  $\text{SiO}_2$ , the percentage of which is to be calculated.

The residue from the hydrofluoric acid treatment consists almost entirely of oxide of aluminum together with ferric and titanic oxides and, in the case of low silica limestones, should not be more than one or two milligrams in amount. Its weight should be added to that of the mixed oxides obtained in the next determination, the simplest plan being to use the same crucible without cleaning it for their ignition.

#### Determination of Iron and Aluminum Oxides.

**Procedure.** Five to ten cubic centimeters of hydrochloric acid are added to the filtrate from the silica above to insure the presence of sufficient ammonium chloride to prevent the precipitation of

magnesium. The total volume should not be more than 150 cc. Dilute ammonia water is then added in very slight excess (42, 6, g) to precipitate the iron and aluminum, when the solution is boiled for a few minutes and the precipitate allowed to settle, after which it is filtered, dissolved in nitric acid and reprecipitated as above in a volume of 100 cc. (42, 5).

The final precipitate is washed free from chlorides with hot water and ignited as described for ferric oxide in Practice II. It consists of  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$  and possible traces of  $\text{FePO}_4$  and  $\text{TiO}_2$ . The weight of the residue from the treatment of the silica is added and the whole calculated as percentage of  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ .

#### Determination of Calcium Carbonate.

**Procedure.** The filtrate and washings from the iron and aluminum hydroxides above, the total volume of which should not be more than 400 cc., are combined in a beaker of suitable size and set over a wire gauze to heat. In the meanwhile a solution of ammonium oxalate is prepared by dissolving 1.5 + g. of the dry salt in 30 to 40 cc. hot water in a small beaker which is also set over a source of heat so that it may be hot when wanted. As soon as the liquid in the large beaker boils, the watch glass is rinsed off, laid aside and the hot solution of ammonium oxalate added in a slow stream with constant stirring (Note 3). This stirring is continued without intermission till the liquid is again seen to boil, when the burner is withdrawn, and after ten to fifteen seconds the stirring stopped. The calcium oxalate precipitated in this way settles rapidly and may be filtered in five or ten minutes.

Owing to the adsorption of magnesium salts this first precipitate must be dissolved and reprecipitated, which can be done by the method of 42, 5, a, using hydrochloric acid as the solvent. Calcium oxalate does not dissolve rapidly in the cold, therefore it is best to heat the mixture after the addition of a few cubic centimeters of acid and add more only if necessary. The acid solution is caused to flow over the sides of the beaker to dissolve any adhering precipitate after which it is diluted if necessary to 100 to 150 cc.

Another method of procedure is to pour the supernatant liquid through the filter as closely as possible without disturbing the

precipitate which is then washed once or twice by decantation (58) using 25 to 30 cc. of hot water. The washing is accomplished by stirring up the precipitate with the water, letting it settle a minute or so and then pouring the liquid through the filter without waiting for it to become perfectly clear. The beaker containing the filtrate and washings is then covered and set aside and the one with the precipitate placed under the funnel. Sufficient warm, dilute hydrochloric acid to dissolve the calcium oxalate is now poured through the filter which is in turn washed with hot water and preserved for the final filtration. (Note 4.)

The reprecipitation is brought about as follows (Note 5): Between one and two tenths of a gram of dry ammonium oxalate is added to the acid solution of the precipitate obtained by either of the methods above and then ammonia till a slight permanent cloudiness is produced. The beaker is now set over a wire gauze and the contents heated to boiling, when 2 to 3 cc. ammonia are again added and the heating continued, this time with constant stirring (Note 3), till the boiling point is reached, when another small portion of ammonia is added, the liquid again boiled and so on till the solution reacts alkaline to litmus paper (Note 6). It is then brought once more to boiling after which it may be set aside to settle and is ready to filter in a few minutes. The original filter is used and the precipitate washed free from chlorides (Note 7) with hot water containing two or three grams of ammonium oxalate per liter. It may be ignited by either of the following plans.

(a) Ignition as Oxide. The method of 60 is followed, the ignition being finished over the blast and continued till constant weight (59,5) is reached. The resulting CaO is very hygroscopic, therefore the lid must be weighed with the crucible and the plan given in 33 used. (See Note 8.)

(b) Ignition as Sulphate. This may be done equally well in porcelain or platinum and consists in transforming the oxalate into the sulphate. For this purpose the filter and precipitate are first dried and the filter burned separately (61). The ash and the dry oxalate are combined in a weighed crucible and thoroughly moistened with concentrated sulphuric acid but avoiding an excess. The crucible is then heated according to 62 a or b till no more white fumes of  $\text{SO}_3$  are seen, when the ignition is completed by

placing the burner directly under it and maintaining a full red heat for ten minutes. (See Note 8.)

From the weight of CaO or CaSO<sub>4</sub>, as the case may be, the percentage of calcium carbonate is calculated.

#### Determination of Magnesium Carbonate.

**Procedure.** The first filtrate and washings and the second filtrate and first three or four washings (Note 7) from the calcium oxalate precipitates above are combined for the precipitation of the magnesium. The volume should not be more than 800 cc. The solution is acidified with hydrochloric acid and a large excess (Note 9) of the precipitant added—4 g. sodium ammonium phosphate or 6 g. sodium hydrogen phosphate. Either salt may be used, the portion being dissolved in a little water. Precipitation is then brought about by adding ammonia solution slowly with constant stirring till the liquid smells strongly of the gas (42, 6, f). A copious precipitate of magnesium ammonium phosphate will be produced if the amount of magnesium present is large. In the case, however, of nearly pure limestones containing only one or two per cent. of magnesium carbonate, no precipitate may appear till after several hours standing. Whether a precipitate appears or not, about 10 cc. ammonia solution in excess are added and the mixture again stirred, after which it is set aside for at least 12 hours before filtering.

The precipitate so obtained is impure but contains all of the magnesium. It is filtered and transferred with dilute ammonia (Note 10) to the paper where it is washed once or twice and is then dissolved according to 42, 5, b in dilute hydrochloric acid—one part acid to five parts water. A little of the acid is first put into the large beaker in which the precipitation was originally made and caused to flow over the sides to dissolve any adhering solids. This is then poured through the filter and the beaker washed out with water. Fresh acid sufficient to complete the solution of the precipitate is now dropped around the edge of the filter which is finally to be washed thoroughly and may then be discarded.

The volume in which the second precipitation should be made is governed by the amount of precipitate and ranges from 300 cc. in the case of a dolomite with 40% or more of magnesium car-

bonate to 50 cc. when only 1 to 2% is present. The bulk of the first precipitate enables the proper estimate to be made.

The precipitation is brought about by adding ten to fifteen milligrams of phosphate to the acid solution, after it has been diluted to the proper volume, and then ammonia solution drop by drop with constant stirring till the odor of the liquid indicates an excess. The stirring is continued for a minute or so after which the solution is set aside for four hours when it may be filtered. It is washed with dilute ammonia (Note 10) till free from chlorides. When the washing is complete the filter and precipitate are moistened with a few drops of a saturated solution of ammonium nitrate made alkaline with ammonia. This aids in the oxidation of the carbon of the filter during ignition.

Magnesium ammonium phosphate is difficult to ignite owing to the slowness with which the carbon burns away. A porcelain crucible should be used according to the method of section 60 and when the paper is all consumed the ignition is carried to constant weight at the full temperature of the blast lamp. As a rule it will be found difficult if not impossible to burn off all the carbon with a Bunsen burner and it is therefore permissible to complete this part of the ignition with the blast lamp but with a relatively small flame, the highest temperature being used only after the black has disappeared (Note 11).

The resulting product is  $Mg_2P_2O_7$  from which the percentage of  $MgCO_3$  is calculated (Note 12).

**Notes.** 1. When a strong mineral acid is added to a solution of a silicate, as for example the sodium silicate of the fusion above, the silicic acid is set free in the colloidal form and, if much is present, immediately begins to precipitate under the influence of the excess of acid and salts (45.5). The precipitation, however, is not complete without evaporating the solution to dryness. The residue so obtained consists of the insoluble silicic acid and salts of the metals present, such as iron, aluminum, calcium, magnesium and the sodium from the carbonate used in making the fusion. No definite formula can be assigned to the silicic acid as it exists after the evaporation and subsequent treatment. It is a gelatinous material which may be looked upon as the normal acid,  $Si(OH)_4$ , which has been largely but not entirely dehydrated.

It is probable that any strong mineral acid will displace the silicic acid from its salts but as a matter of experience only two are used, hydrochloric and sulphuric. Of these, sulphuric acid is the better since evaporation to the point of white fumes more completely dehydrates the silicic acid than can be accomplished by evaporation to dryness with hydrochloric acid. It is, however, seldom used on account of the insolubility of the resulting sulphates of the alkaline earths. Hydrochloric acid is therefore almost universally employed as in the method described above.

Quantitative precipitation of the silicic acid and consequent sharp separation from the metals can be accomplished only by proper regulation of the temperature at which the residue from the evaporation is dried and by making at least two evaporation with intermediate filtration. Older methods frequently call for drying the residue at temperatures above 100°, from 110 to 130° being most frequently named. With certain samples this may at least do no harm, but with others the temperature of the water bath or steam box is preferable. A certain amount of silicic acid which separates on the first evaporation always dissolves when the residue is treated with hydrochloric acid. This may reach 4 to 5% of the total amount present and is therefore seen to be too large to neglect (78). If now this first portion be filtered off and the filtrate again evaporated, the amount which will dissolve on treatment of the second residue will be negligible. The intermediate filtration seems to be necessary, as a second evaporation without it does not serve the purpose.

It is sometimes advantageous as a time saving device to make the first evaporation rapidly (64.2) and dry the residue at a higher temperature. This is permissible because all of the silica will be recovered on the second evaporation which must always be finished on the water bath or steam box.

2. Hydrofluoric acid forms with silica the volatile compound  $\text{SiF}_4$ . In the treatment of a silica precipitate a little sulphuric acid is added to prevent the volatilization of fluorides other than that of silicon. The excess of hydrofluoric acid is expelled before the sulphuric on account of its greater volatility, the sulphates remaining being either non-volatile or decomposing to oxides (62).

*The greatest care must be used in working with hydrofluoric acid since burns from it are painful and difficult to heal.*

3. Solutions containing precipitated calcium oxalate must be stirred constantly while being heated, on account of the violent bumping which may take place when the temperature is near the boiling point.

4. Two methods for dissolving the calcium oxalate obtained by the first precipitation are given in the procedure above to illustrate how manipulative details may be varied. The points of each plan should be noted and compared. Still other variations could be introduced.

5. The peculiar method of reprecipitating the calcium oxalate was devised by Richards\* who used it for the separation of calcium and magnesium with one precipitation. Its purpose in the second precipitation as described above is to produce a precipitate of good physical condition for filtering, for, unless the directions are followed practically as given, great difficulty may be experienced in that operation. It is an excellent example of the good results of proper manipulation.

6. Owing to the heavy precipitate, the plan of putting into the solution a piece of litmus paper to indicate the change of reaction will not work well in the precipitation of calcium oxalate, and dipping it into the boiling solution with the hand will be found uncomfortable. If, however, a strip of the red paper be moistened and then grasped with the crucible tongs, the test can readily be made, the tongs being laid across a beaker during the addition of the ammonia. Wetting the paper causes it to stick so that it will not fall off when the tongs are laid down.

If a solution of methyl orange is at hand a few drops may be added to impart a distinct pink color to the liquid. An excess of ammonia is then indicated by a change to yellow. The presence of this substance in no way interferes with the reactions and is perhaps to be preferred to the litmus paper.

7. As a general rule all of the washings from a second precipitation need not be saved for the determination of a constituent in the filtrate. A little consideration will show that the concentration of any substances in the first filtrate must be very low in the second, and that after three or four washings the amount that could remain would be negligible. Advantage is taken of this in the separation of calcium and magnesium.

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\*Richards, McCaffrey and Bisbee, *Zeit. fuer Anor. Chem.* 28, 71.

8. When the amount of calcium precipitate is small, ignition as oxide is greatly to be preferred. Even in the case of a large precipitate, such as is obtained in the analysis of limestones, it serves every purpose when a platinum crucible and a strong blast lamp are available. The time required for reaching constant weight can be reduced by breaking up the lumps of precipitate after the filter is burned. This can be done with a stirring rod which is then wiped with a bit of ashless paper and the piece put into the crucible.

With a porcelain crucible in a clay triangle the rate of heating is so slow that the sulphate method may be considered as good. Students are recommended to try both. It is necessary to dry the precipitate and burn the paper apart, for if they were ignited together, some carbonate and oxide would be formed with which the acid would react so violently as to cause loss. The reaction with the oxalate is slower.

9. The first precipitation of magnesium ammonium phosphate illustrates how a procedure may be varied to suit special conditions. The combined filtrates and washings from the calcium oxalate are of necessity large in volume and in order to obtain a pure magnesium compound with one precipitation it would be necessary to evaporate this large volume of solution to dryness and ignite it to expel the ammonium salts. Another plan would be to concentrate the liquid and make a double precipitation. If, however, this is to be done, the concentration can be avoided by making the first precipitation with a very large excess of reagent and allowing sufficient time for the reaction to go to completion.

10. Most text-books call for the use of 2.5 to 3% ammonia solution for washing magnesium ammonium phosphate. This is now known to be unnecessary. About 10 cc. of strong ammonium hydroxide solution (29% NH<sub>3</sub>) in 500 cc. of water is sufficient. At this dilution it can be used with comfort in an ordinary wash bottle.

11. When magnesium ammonium phosphate is precipitated with PO<sub>4</sub> in excess as in limestone analysis, the precipitate acts on platinum during the ignition and it is therefore better to use a porcelain crucible.

12. At best the magnesium precipitate is not pure magnesium ammonium phosphate, MgNH<sub>4</sub>PO<sub>4</sub>, but contains small amounts

of mono-magnesium ammonium phosphate,  $Mg(NH_4)_4(PO_4)_2$ . This latter salt on ignition changes to magnesium metaphosphate,  $Mg(PO_3)_2$ , which on prolonged blasting is transformed into the pyrophosphate with loss of  $P_2O_6$ . For this reason the precipitate must be heated to constant weight over the blast lamp.

13. The magnesium pyrophosphate can be tested as follows for the presence of calcium: It is dissolved in a little hydrochloric acid and then ammonia added until a permanent precipitate forms. This is dissolved by just sufficient acetic acid for the purpose and the solution filtered if a slight flocculent precipitate remains after the main portion has dissolved. A few drops of strong ammonium oxalate solution are then added which will precipitate any calcium that may be present. The precipitate, if one forms, should be granular in appearance and not adhere to the glass. Otherwise it may consist of magnesium oxalate.

14. If the filtrate from the calcium precipitate stands a long while some magnesium oxalate may separate. In this case the supernatant liquid is poured off as closely as possible and hydrochloric acid added to the solid which will then readily dissolve. If acid were added directly to the whole solution, a much larger quantity would be required.

**General Notes.** 1. When the methods of analysis as described above are applied to a limestone, any phosphoric acid and titanium that may be present are precipitated with the iron and alumina. Strontium comes down with the calcium oxalate. Manganese when present in very small amounts would precipitate with the magnesium. Sodium, potassium, sulphur, organic matter and water entirely escape precipitation.

2. If the determination of the iron is wanted, the two oxides should be precipitated together with macerated paper as described in Practice II. and, after ignition and weighing, are dissolved and the iron titrated. (See page 172).

3. For many technical purposes an accurate determination of the silica is not necessary, in which case the matter insoluble in acid is filtered off, ignited and weighed, being called silicious residue. For this purpose the sample is brushed immediately into a casserole where it is treated with acid and the mixture evaporated to dryness at once without filtering; or the casserole may be covered with a watch glass and the solution boiled down over a free

flame (See 64, 2). The residue so obtained is treated with hydrochloric acid exactly as described above for silica and the insoluble material consisting of sand, clay and a little pure silicic acid filtered off, ignited and weighed. It need not be treated with hydrofluoric acid.

The subsequent determinations are practically as described above excepting that, as a rule, no precipitates are dissolved and reprecipitated.

4. If the limestone is not too silicious in character, for example does not contain above 15%  $\text{SiO}_2$  and not over 6% of iron and alumina, simple ignition will as a rule so decompose it as to render it soluble in acids. The procedure is as follows: The sample is weighed directly in a platinum crucible which is then covered with a closely fitting lid and heated cautiously at first over a Bunsen burner. Specimens high in magnesium should receive special care to prevent loss due to the sudden expulsion of carbon dioxide. The heating is finally continued for ten or fifteen minutes at the highest temperature of the blast lamp. The residue remaining will be greatly reduced in bulk and be sintered or clinkered together. It should be transferred to a dish or casserole and moistened with water. Any portions not readily detachable from the crucible may be removed with a little hydrochloric acid. The whole mass in the casserole is finally covered with dilute acid and warmed, the lumps being broken up with a stirring rod. Everything should dissolve excepting a little flocculent silicic acid, precipitated by the hydrochloric acid. If no gritty particles can be felt by the stirring rod the decomposition is complete. The sample is now in hydrochloric acid solution and ready for the succeeding steps in the analysis.

The chemical changes brought about by the ignition are complete loss of carbon dioxide with consequent formation of oxides of calcium and magnesium. Any organic matter present is destroyed and all water expelled.

In the case of those samples to which it will apply, this method is preferable to the sodium carbonate fusion. Students should, however, use the fusion method because it is the more important owing to its more general application. If it should be necessary to make more than two analyses the later ones may be decomposed by ignition.

#### IV. PREPARATION OF A STANDARD HYDROCHLORIC ACID SOLUTION AND A HALF-NORMAL ACID SOLUTION.<sup>1</sup>

##### The Standard Acid.

The use of acid and alkaline solutions is so extensive in volumetric analysis and the direct standardization by gravimetric methods so time consuming that every well regulated laboratory aims to have on hand one such solution the strength of which has been determined with great care so that it can serve as a standard for the others.

The following considerations govern the choice of such a solution: It should be an acid rather than an alkali on account of the lesser action on glass (64, 3). Among the acids one should be chosen that is stable towards ordinary laboratory conditions, especially towards light and air, and the chemical nature of which permits accurate standardization by direct gravimetric methods. Finally, if possible, choice should be given to one the common salts of which are soluble. On subjecting the acids, hydrochloric, nitric and sulphuric, to these tests, hydrochloric will be found the one that meets most of them.

The strength of such a standard is also of importance and when the considerations outlined in 98, 1 are applied, it will be found that from 0.2 to 0.3N meets the requirements. No attempt should be made to make it exactly a simple fraction of normal as this introduces an extra operation. The strength should fall within the limits named above and is then determined accurately, after which the solution should not be changed.

In a general laboratory, then, there would be prepared 5 or 6 liters of a hydrochloric acid solution approximately 0.25N and its exact strength determined by two or more independent methods, for example, titration against sodium carbonate (see below) and precipitation with silver nitrate. (See determination of chlorine in barium chloride, p. 135.) Such a standard is carefully preserved

<sup>1</sup>Before beginning volumetric work, the student should calibrate a burette, a 50 cc. or 25 cc. pipette and a liter or 500 cc. flask, according to the directions under calibration.

(99) and extra care is used in handling it to prevent contamination. It is usually supplied with a lengthy label giving its strength in various terms and equivalents in order to facilitate calculations. This solution is kept solely for standardizing other acids and alkalis that are then employed in analysis.

For students' practice work 1500 to 2000 cc. (98, 5) approximately 0.25N hydrochloric acid should be prepared and the strength determined by titration against sodium carbonate as described below. By indirect comparison with this solution a correct 0.5N acid is then made to be used subsequently in the analysis of soda ash in Practice V. The standard acid is to be preserved for future use. It could of course be employed in the analysis of the soda ash but a large part of the value of the practice work would then be lost, namely, the indirect comparison of two solutions of the same reaction and the preparation of a solution of a certain exact strength.

Sodium carbonate as a standard substance in determining the strength of acid solutions has been in use many years and is still one of the best in spite of the troublesome manipulation required to obtain it pure. The fact that it must be dried to constant weight immediately before use is perhaps one of the reasons for the uniformly good results attending its employment. (See also Note 7.)

It should be prepared by heating the purest bicarbonate short of redness to expel the water and excess of carbon dioxide (Note 1). In extremely refined work the bicarbonate should be made by saturating a strong solution of normal sodium carbonate with carbon dioxide, filtering the precipitate and, after dissolving it in a little hot water, again precipitating in the same way. For students' use, however, the best bicarbonate (Kahlbaum's or the "analyzed" brands of American manufacturers) will serve every purpose.

**Procedure for the Standard Acid.** The preliminary solution should be prepared from the strong acid as obtained at the store room. This may be assumed to have a specific gravity of 1.20 and to contain 39% by weight of HCl. In calculations of this sort specific gravity may be called the same as weight in grams per cubic centimeter. The problem then is as follows: 1 cc. of strong hydrochloric acid weighs 1.20 g. and contains 39% of actual HCl. How many cubic centimeters must be diluted to make n cc. of

0.25N? (See 103, 2.) Since only approximate results are obtained by this method of calculation, the cylindrical graduate may be used for measuring the acid and the liter flask for getting the volume of the water. (See 98, 4.)

The next step in the procedure is to calculate the amount of pure  $\text{Na}_2\text{CO}_3$  to be used in one titration (98, 2 and 107). About ten times the equivalent quantity of bicarbonate is then roughly weighed into a clean casserole in which it is heated 10 to 15 minutes over a flame four or five inches high (Note 2). The casserole should be held in the hand and kept moving while in contact with the flame, so that no part of it becomes red hot. From time to time the contents should be stirred with a glass rod which can be left in during the heating. When the excess of water and carbon dioxide has been driven out the resulting, practically pure sodium carbonate is put into a clean, dry bottle where it will keep indefinitely.

The final quantitative drying of the portions for titration is accomplished in small weighing flasks provided with ground glass stoppers (Note 3). These are cleaned, dried, cooled in a desiccator (Note 4) and weighed. The proper amount (98, 2) of the pre-dried carbonate above is then added, this being most conveniently accomplished by putting on extra weights immediately after the weighing of the empty flask and then restoring equilibrium by adding sodium carbonate. Nothing is gained by attempting more than a rough approximation at this point.

The last traces of water are driven out by heating the flask in a sand bath as follows: A flat, iron dish filled with sand is set on a tripod or ring stand and heated with the full flame of a Bunsen burner. (The desk should be protected with a piece of asbestos.) The weighing bottles containing the carbonate to be dried are imbedded about an inch in the sand. The stoppers are laid on sideways to permit the water vapor to escape and the heating continued for at least 20 minutes. The drying is hastened if the carbonate is gently shaken up once or twice, which can easily be accomplished by handling the flasks with the crucible tongs, previously warmed.

At the end of the heating the flasks are placed in a desiccator (Note 4) with the stoppers still lying loosely on top, care being taken to brush or wipe off any sand that may be adhering to the

outside. When cool the desiccator is opened and the stoppers quickly inserted. The flasks can now be weighed without danger of taking up water. In this manner the heating is continued till constant weight (59, 5) is reached. The shaking should, however, be omitted after the first heating.

The carbonate is now ready for solution and titration but owing to the small size of the weighing bottle it must first be transferred to a larger vessel, a beaker or flask, of about 300 cc. capacity. This is best accomplished by first dissolving the salt in the weighing bottle and then transferring the liquid. (See section 65.) The greatest care must be used in this operation since the loss of a single drop would be fatal. A funnel set in the receiving flask will help. It must, however, be rinsed off carefully, not omitting the outside of the stem, when it is removed. The sides of the flask must also be rinsed down. Methyl orange (III, 2) is now added and the solution titrated with the standard acid, the temperature of which should be taken (Note 5). It is well before attempting the titration to review section 113. At least three closely agreeing results should be obtained, from the average of which the following should be calculated:

- I. The normality of the solution, through four decimals.
- II. The amount of HCl per cubic centimeter, through six decimals.
- III. The number of cubic centimeters of normal solution to which 50.00 cc. of the standard acid are equivalent, through two decimals.

The results of these calculations together with the other data as indicated below should be arranged neatly in the form of a label that is then to be attached to the bottle containing the acid. Such a label should read as follows:

Standard HCl  
O.\_\_\_\_\_N  
1.00 cc. = O.\_\_\_\_\_g. HCl.  
50.00 cc. = \_\_\_\_\_.\_\_\_\_cc. N.  
Standardized by titrating Na<sub>2</sub>CO<sub>3</sub>.  
Methyl orange indicator, first color change.  
Temp. of standardization = \_\_\_\_\_ degrees.  
Date \_\_\_\_\_ Signed \_\_\_\_\_.

### The Half-Normal Acid.

The two important points in this part of the laboratory practice work are, (1) the standardization of a solution by means of another of the same reaction, and (2) the preparation of a solution of a certain exact strength.

The general method involved in the comparison of two solutions of the same reaction, is to prepare a third solution of the opposite reaction and titrate measured portions of it with both of the others. This gives the values of the two in terms of the third and hence their relation to each other. The exact strength of this third solution need not be known but for convenience sake it should be adapted to that of the others.

The general method of preparing a solution of a certain exact strength is described in section 98, 3.

In the application of the above general principles to any particular case, much can be accomplished, especially in saving calculation, by suitable arrangement of the experimental work. The student should note the procedure below and reason out its general application.

**Procedure.** A quantity (98, 5) of hydrochloric acid solution somewhat stronger than 0.5N is first prepared from the strong acid as described above. This may be called Solution A. About a liter of sodium carbonate solution (Note 6) is then made, stronger than the Standard Acid but not so strong as Solution A. This may be called Solution B.

Several 50 cc. pipettefuls of the Standard Acid are now titrated with the sodium carbonate and the average of the closely agreeing results taken. This gives the relation, 50.00 cc. Standard Acid = n cc. Solution B. Three or four portions of n cc. of the sodium carbonate solution are now measured by means of the burette into clean flasks or beakers. The burette is then charged with the acid solution A and the several portions of n cc. of B are titrated, thus giving the relation n cc. B = m cc. A, the average being taken as the final value. It will be observed that the experimental work is so arranged that the same volume of alkaline solution B is used in both cases. Without any calculation it is then apparent that 50.00 cc. Standard Acid = m cc. Acid A. Reference should now be made to the label of the Standard Acid to find the

number of cubic centimeters of 0.5N solution corresponding to 50.00 cc. Call this r cc. If Solution A has been made stronger than 0.5N, m will be less than r and it is evident that if m cc. of Acid A be diluted to r cc. it will be exactly 0.5N. Acid A should therefore be diluted at the rate of m cc. to r cc.

After the dilution of Acid A it should again be compared with the Standard Acid in order to verify the work. With this in view it is well to have measured out several extra portions of the alkaline solution above. They can be preserved in any sort of vessel and rinsed subsequently into a flask or beaker for titration.

**Notes.** 1. The normal sodium carbonate,  $\text{Na}_2\text{CO}_3$ , is not used because the history of its drying or calcination is not known. Having been done in large lots and with no reference to its use in such refined work as standardization, it is possible that portions may have been overheated.

2. Bicarbonate could be dried directly in the flasks but it would obviously take much longer. The preliminary heating as described above is easy to carry out and greatly reduces the time required to bring the material to constant weight.

3. The advantage of glass stoppered weighing bottles lies in the fact that they can be closed, thus preventing access of moisture from the air during the operation of weighing. If such flasks are not available small, plain ones, about 25 to 75 cc. in capacity, can be employed. A crucible lid used as a cover greatly reduces but does not entirely prevent the taking up of water from the air. The trick of weighing as described in section 33 should be employed.

4. The method of section 31 can not be used in weighing the flasks because they must be cooled before the stoppers are inserted. If this were not done the reduced pressure on the inside would cause them to stick so tightly they could not be withdrawn. Owing to the hygroscopic character of the sodium carbonate, the cooling of the open flasks must take place in a dry atmosphere (desiccator). The precautions referred to in 31 are also more applicable to larger vessels than small weighing bottles.

5. The refinement of taking the temperature into account is explained by the importance of the work of standardization. (See also 93, 4.) Section 100 discusses the effect of temperature changes on standard solution.

6. The sodium carbonate used in "fusions" should be employed for the intermediate alkaline solution in the preparation of the 0.5N acid. It would be a waste of time and good material to use the pure bicarbonate for this purpose.

7. In addition to the use of sodium carbonate and precipitation by silver nitrate, many other methods for the standardization of a hydrochloric acid solution can be used. Ambitious students will be interested in looking up some of these in the larger textbooks or better still in the current literature. Consult Chemical Abstracts under the titles Acidimetry and Alkalimetry, the general terms used to designate the employment of standard acids and alkalis in quantitative chemical measurements.

## V. DETERMINATION OF THE TOTAL ALKALINE STRENGTH OF SODA ASH.

Soda ash is crude, calcined, sodium carbonate and may contain impurities such as sodium sulphate, chloride and hydroxide. Simple titration with acid will therefore not give the percentage of carbonate because some of the impurities, notably the hydroxide, also neutralize acids. The impurities, however, are small in amount and, as a rule, it is a matter of indifference in the commercial use of the material whether its alkalinity all comes from the sodium carbonate or in part from the hydroxide. For practical purposes therefore a determination that measures the total alkalinity is sufficient.

When such a mixture of substances is titrated, however, it is necessary to calculate the result in terms of one of them, and in case of soda ash, the alkalinity, whatever may be its source, is considered as sodium carbonate. This is a situation of rather frequent occurrence in quantitative analysis and must be clearly understood. The following example will illustrate the point: A mixture of 0.7959 g.  $\text{Na}_2\text{CO}_3$ , 0.0401 g. NaOH and 0.1540 g. inert material is titrated with 0.5N acid. A calculation will show that 31 cc. will be required. If now the composition of the mixture is unknown, the whole alkalinity is assumed to be caused by sodium carbonate, the amount of which, equivalent to 31 cc. 0.5N, is calculated. This is 0.8224 g. which means that 0.8224 g.  $\text{Na}_2\text{CO}_3$  has the same alkaline strength as 0.7959 g.  $\text{Na}_2\text{CO}_3 + 0.0401$  g. NaOH.

The amount of water in soda ash is variable so that samples taken from the same lot at different times will not agree. To obviate this it is customary to dry the material to constant weight at 110° (see 38 and 39).

**Procedure.** Two plans may be followed in weighing the sample for analysis: (1) About a gram is dried to constant weight at 110° in a small flask or other suitable container, or (2) a larger amount is dried as above, dissolved, diluted in a graduated flask and an aliquot part taken for the analysis (see 37, 4). In case this latter plan is used the amount of soda ash must be so adapted to the size of the flask and pipette at hand that approximately a gram will be contained in 50 or 100 cc. An excellent

combination is to dilute 4 or 5 g. in a 200 or 250 cc. flask. A 50 cc. pipette will then measure the desired amount.

The weighing in the case of the larger amount need not be made as accurately as in case (1). See 78 for general method of answering the question, how accurate.

In case the first method is used, the accurately weighed portion is dissolved in 75 to 100 cc. of water, and titrated (113) with the 0.5N acid, methyl orange being used as indicator. When the second method is employed, the aliquot portion of the solution is titrated directly.

Some samples contain sufficient insoluble material to make the solution cloudy. In this case it must be filtered and the filter and residue washed, the washings being combined with the filtrate. A slight turbidity, however, that will not interfere with the end-point may be disregarded.

If the second plan be employed, filtration can be avoided by letting the contents of the graduated flask stand till clear. The portion pipetted out can then be titrated at once. If the solution is to be filtered it had better be done before the dilution in the flask.

As stated above, the results of the titration are expressed in terms of  $\text{Na}_2\text{CO}_3$ , the percentage of which in the dried ( $110^\circ$ ) sample is calculated.

**Special Note.** Before beginning the next assignment of laboratory work, students should refer to page 176 and note that the thiosulphate solution called for there is to be made up ten to fifteen days in advance of its standardization.

## VI. PREPARATION OF TENTH-NORMAL POTASSIUM DICHROMATE SOLUTION.

A solution of potassium dichromate, though a strong oxidizing agent, is perfectly stable under ordinary laboratory conditions. It is unaffected by light, is not acted upon rapidly by organic matter, can be used in contact with rubber, and does not act upon dilute hydrochloric acid. This latter point is of great advantage since this acid is so frequently used as a solvent.

The salt  $K_2Cr_2O_7$  is easily obtained pure and if recrystallized and dried, is one of the best standard substances to be used in determining the exact strength of oxidizing and reducing solutions. Its own solutions are therefore prepared by dissolving an accurately weighed portion. In the following practice work, however, the strength of the solution will be checked by comparison with "pure" iron wire. Practice of this sort, the making of an accurate chemical measurement by two independent methods, is of great value to a student and should be given his best care and attention.

The chief objection to be made to standard solutions of potassium dichromate is the fact that no convenient indicator has as yet been found for it. In the example cited below, the titration of iron, small portions of the solution are removed from time to time towards the end of the reaction and tested for ferrous salt by means of ferricyanide of potassium. This, even in the presence of a large excess of ferric iron and chromium salts, gives a blue color with ferrous iron. As little as 0.0003 g. Fe in 100 to 150 cc. of solution can be detected in this way. The removal of portions of the solution does not materially affect the result since in the first place but a small fraction of the total volume is removed and this only towards the end of the titration when the solution is exceedingly dilute with reference to the iron still remaining unacted upon.

Iron wire as a standard for determining the strength of oxidizing solutions is not an ideal one in all respects, for it lacks the quality of being pure in the chemical sense. Even that prepared and put on the market for standardizing (and no other should be used) contains appreciable traces of carbon, silicon, phosphorus, manganese and perhaps other common impurities of

commercial iron, for which a correction must be applied. This correction is usually supplied by the manufacturer and for beginners' practice work may be accepted as correct. As a rule it amounts to 0.2%, that is, the wire is 99.8% iron.

If the correction is to be found by the chemist it is done by dissolving a large quantity of the wire and determining the percentage of each impurity, the sum of which is then subtracted from 100% to get the amount of pure iron.

The great advantage of the iron wire as a standard lies in its permanence and ease of handling.

**Procedure.** Recrystallizing and Drying the Salt. The starting point should be the c. p.  $K_2Cr_2O_7$ . Four or five times as much as is subsequently to be used (98.5) is dissolved in the smallest possible quantity of hot water in a flask of such size that the solution should not more than half fill it. This hot solution is then cooled in a stream of tap water, with constant rotation of the flask, the rapid cooling and agitation causing the dichromate to separate in small crystals, the so-called crystal meal.

The separation of the crystals from the mother liquid is accomplished by throwing them onto a Witt plate in a funnel supported in a suction flask. When the mass has been transferred, the suction is turned on and continued as long as liquid is seen to flow from the funnel (Note 1).

The moist crystals are then put into a clean casserole and heated cautiously to drive off the water. If the work can be so arranged, the casserole may be left on the water bath or steam box. When the excess of water is driven out and the crystals appear dry, the heating should be continued for fifteen to twenty minutes at a somewhat higher temperature over a sand bath or iron plate heated from below. During this second heating the salt should be stirred frequently and not be allowed to become soft or sticky. Only a relatively low temperature is needed. If a suitable drying oven is available, heating at  $130^\circ$  will suffice. A higher temperature, even up to the melting point, does not, however, decompose the salt.

During the whole operation of crystallizing, filtering and drying, the dichromate should be carefully protected from dust.

The finished product is finally transferred to a clean, dry bottle. It is not hygroscopic and may be weighed in open vessels.

Preparation of the 0.1N Solution. The requisite quantity (104) of the dry salt is weighed accurately, dissolved in a few hundred cubic centimeters of water and then diluted to the proper volume (98, 5). The best procedure for students who have only a liter flask for the measurement of large volumes of liquid, is to plan for 2000 cc. of solution. The weighed salt is then transferred directly into the measuring flask and dissolved. The flask must not be more than half full so as to permit rotating the liquid to hasten solution. When everything is dissolved it is diluted to the mark and mixed (98, 4). This double strength solution is then transferred to a dry bottle, and the flask again filled with water and the contents mixed. The second liter of liquid is also added to the stock bottle and thoroughly mixed with the first. If the liter flask had been drained carefully (85, 2) each time, the small amount retained after the second emptying can be disregarded. It can, however, be recovered by pouring the solution back and forth a number of times between the stock bottle and flask (see also 98, 3, 6).

Comparison with the Iron Wire. The approximate weight per inch of the wire and the weight required for one titration are first found. (See 98, 2 and 107, 2.) A piece is then taken about two inches longer than will be wanted and cleaned by grasping one end and drawing the rest through a fold of fine sand paper or emery cloth. This effectually removes all rust. Adhering sand is then wiped off with a piece of filter after which the wire is cut into lengths of about one inch, the pieces being received on a clean sheet of paper. The end that was held in the fingers is rejected. The number of these short pieces that most nearly makes the desired amount for one titration (98, 2) is then accurately weighed and dissolved as follows:

Five or six cubic centimeters of strong hydrochloric acid are diluted to about 150 cc. in an Erlenmeyer flask and the solution boiled for five or ten minutes to expel the dissolved air. The flask is then removed from the heat and the weighed portion of iron added. A small funnel is set in the mouth to serve as a trap to prevent loss by spraying. Heat may again be applied if, after some minutes, the rate of solution becomes too slow. The iron may dissolve as rapidly as possible so long as there is no danger of loss through spray carried out by the escaping hydrogen. The iron dissolves to ferrous chloride, the completion of solution being

recognized by the cessation of small bubbles rising from particles of solid. Black specks from which no bubbles rise are carbon.

When solution is complete the inside and outside of the funnel and the inside of the flask are rinsed down with hot, boiled water. (Careless use of cold water would crack the funnel.) The titration should be made at once as the iron oxidizes slowly on exposure to air.

**Titration of the Ferrous Chloride Solution.** A solution of ferricyanide of potassium should be made by dissolving a crystal about the size of a pin head in 25 to 30 cc. of water. It is well to start with a somewhat larger piece and rinse it several times with water to dissolve the outer portion and remove any ferrocyanide that may have formed. It must be freshly prepared for each titration as it is not stable (Note 2).

The titration may be made in the flask or the iron solution can be transferred to a casserole. Section 113, especially 113, 2, should be reviewed. The following details for the peculiar endpoint of this reaction are suggested: A number of drops of the ferricyanide solution are first spotted over a porcelain plate (Note 2) and then from time to time as the addition of dichromate progresses, a drop of the iron solution is removed and allowed to fall onto a drop of the ferricyanide. The bright blue color produced as long as much ferrous salt is present gradually gives place to a paler shade as the oxidation proceeds. The final tests when very near the end-point are best made in the reverse order. A large drop of the iron solution is placed on the plate and a drop of the indicator solution allowed to fall into the middle of it. If, after twenty seconds, no blue color can be seen at the junction of the two liquids, the reaction may be considered complete. Too long standing would develop a blue color owing to the decomposition of the ferricyanide (Note 3).

Three or four titrations should be made and from the average of the closely agreeing results the strength of the dichromate is calculated. This is then compared with the value determined by the amount of salt dissolved (See 115).

**Notes.** 1. For drying crystals by suction an apparatus after the plan of that illustrated in section 55 should be used. Instead of the support for the Gooch crucible an ordinary funnel is set in the stopper. Since it is desirable to avoid as far as pos-

sible any admixture of shreds of filter paper, a perforated porcelain plate (Witt plate) is put into the funnel to retain the solid. Usually a good deal of material runs through at first but this can be recovered by pouring through a second time. The crystals are in this way made to serve as their own filtering medium. If the holes in the plate are too large it may be necessary to lay a piece of filter paper on top. If this is done the paper should first be laid on a watch glass and the loose shreds washed off with a stream from the wash bottle. The so-called hardened filters may also be used in the ordinary way for filtering when suction is to be applied.

2. The tedium of a dichromate titration can be lightened somewhat by providing two pipettes made by drawing down slightly the end of a small glass tube. One of these should be used in the ferricyanide solution for conveying drops to the plate and the other one in the iron solution being titrated. An ordinary white dinner plate serves admirably for making the tests. White, glazed paper can also be used.

Beginners will of course require several platefuls of tests to hit the end-point in the first trials, but skill will come rapidly with practice. The method is as accurate as the average titration and with care the disappearance of the blue color can be told to within a drop of the standard solution. The time of waiting is important, it being better to use a watch rather than to try to guess twenty seconds.

## VII. THE DETERMINATION OF IRON IN IRON ORE.

Volumetric methods are almost universally employed in the determination of iron in its ores. After the solution of the sample, it is brought to the ferrous state by appropriate reducing agents such as nascent hydrogen, hydrogen sulphide or stannous chloride and then titrated with potassium permanganate or dichromate. In this practice the dichromate method will be employed. The iron is reduced with a slight excess of stannous chloride and this excess removed by means of mercuric chloride with which it forms insoluble mercurous chloride. The solution may then be titrated with standard dichromate as described in the preceding practice. Neither the solid mercurous chloride nor the excess of mercuric salt is acted upon.

The reactions involved are as follows:

- I.  $6\text{FeCl}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} = 6\text{FeCl}_3 + 2\text{CrCl}_3 + 2\text{KCl} + 7\text{H}_2\text{O}$ .
- II.  $3\text{FeCl}_2 + 2\text{K}_2\text{Fe}(\text{CN})_6 = \text{Fe}_3(\text{Fe}(\text{CN})_6)_2 + 6\text{KCl}$ .

For the reaction between stannous chloride and mercuric salt, see 104, 5.

In addition to the standard dichromate there will be required solutions of mercuric chloride and stannous chloride, as follows:

Mercuric Chloride Solution: About 7 g. of the salt are dissolved in 150 cc. of water. This is practically a saturated solution at room temperature.

Stannous Chloride Solution: Fifteen grams (roughly weighed) of the salt together with about a gram of pure metallic tin are heated with 40 cc. of water and 10 cc. of concentrated hydrochloric acid. Owing to the readiness with which this solution takes up oxygen from the air, it must be preserved in a tightly stoppered bottle.

**Procedure.** About 0.5 g., or a factor weight (107, 7), of the ore, ground fine in an agate mortar (37, 3) is weighed into a small beaker and covered with 25 to 30 cc. of concentrated hydrochloric acid, 1.20 sp. gr. One cubic centimeter of stannous chloride solution (see above) is then added, the beaker covered with a watch glass and heated on a hot plate or wire gauze so

the acid just boils. If the solution becomes yellow or brown due to the formation of ferric chloride, more stannous chloride should be added (Note 1). When an excess of the tin salt is present the completion of solution can be recognized by the disappearance of the brown cloud of ferric chloride over the silicious residue. The observation is best made by looking at the bottom of the beaker. When solution is complete, the watch glass is rinsed off, the acid diluted somewhat and the residue filtered and washed till the washings no longer taste sour.

Unless the character of the ore is known it is unsafe to assume that the residue of sand and clayey matter, even when it is light in color, contains no iron; therefore at least one such residue from each general sample of ore must be ignited and fused (41, 4). The fusion must, however, be conducted with great care to avoid the introduction of platinum (Note 2). The fused mass is dissolved directly in dilute hydrochloric acid (41, 2) and the iron determined in it separately to see whether there is enough present to warrant a fusion in the case of each analysis for, if it is found to contain practically no iron, subsequent samples of that ore need not be fused. In case, however, the silicious residue does carry more iron than may be neglected, the fusion must be made for each determination, but it is not necessary after the first time to titrate it separately. After solution in a little dilute hydrochloric acid it is combined without filtering with the main solution of the ore and the two, now containing all of the iron, titrated together.

In the event that the silicious residue does not retain iron, the acid solution of the ore need not be filtered as the insoluble matter in no wise interferes with the subsequent operations.

When, as described above, all of the iron has been brought into solution, the color of the liquid must be noted. If yellow or brownish red it is ready for the final reduction with stannous chloride preparatory to titration. If, however, the liquid is colorless, it shows that some of the stannous chloride used in dissolving the ore still remains. This is oxidized by adding dilute solution of potassium permanganate (Note 1) drop by drop with constant stirring, till the liquid acquires a permanent yellow color. It is then ready for the final reduction of the iron as described below.

The solution is transferred to a casserole, diluted to about 100 cc. and 5 to 6 cc. concentrated hydrochloric acid added. It is

then brought to boiling and the iron reduced with stannous chloride solution, a drop at a time, till the yellow color of the ferric chloride disappears and the liquid is colorless like water, or at most has a slight greenish tinge. It is then cooled rapidly by placing the casserole in a larger vessel with cold water and when cool or at least only slightly warm, 15 cc. of the mercuric chloride solution are poured in all at once and stirred rapidly through the liquid. A white, silky-like precipitate should form. If it is at all gray or dark colored it indicates that too much stannous salt was present or the solution was too hot, thus occasioning the reduction of some metallic mercury. If this happens the determination is ruined.

If the precipitate remains white, three or four minutes should be allowed for the completion of the reaction between the stannous and mercuric salts after which the titration of the iron should be carried out at once as described in Practice VI, the results being reported as percentage of iron.

**Notes.** 1. The iron in most ores is in the ferric state and therefore dissolves in hydrochloric acid as ferric chloride. According to the general law of mass action the rate of solution decreases as the concentration of the products of the solution increases. In dissolving an iron ore the reduction of the rate of solution is prevented by changing the ferric salt to the ferrous as fast as formed, by means of the stannous chloride. On account of the difference in color between the ferric and ferrous chlorides this plan also enables one to note when the solution of the ore is complete.

Since it would be tedious to add the tin salt a little at a time as needed to reduce the iron, an excess is put into the solution at once and, at the conclusion of the operation, any that remains, indicated by a colorless solution, is destroyed by means of potassium permanganate. This acts first on the stannous chloride, oxidizing it to stannic chloride and then on the ferrous iron which it changes into ferric chloride. The appearance of the yellow color of this salt therefore indicates that all of the stannous compound is destroyed. The presence of a little ferric iron does no harm as it is afterwards reduced by the cautious addition of more tin solution.

The student should distinguish sharply between the two uses of stannous chloride in this determination of iron. In the first case it merely promotes the solution of the ore. Permanganate in-

stead of mercuric salt is used at this point for oxidizing any excess because there is no means of knowing how great the excess may be. If there should be much present, metallic mercury would precipitate and ruin the determination. The second use of the stannous chloride is to reduce the iron to the ferrous state preparatory to titration. For this purpose it is added to the hot, strongly acid solution till the disappearance of the yellow color of ferric chloride shows that all the iron is reduced. The excess of acid increases the intensity of color of the ferric chloride and later, during the titration, prevents the formation of basic salts.

2. Platinum is slightly acted upon by melted sodium carbonate and therefore a trace may get into the solution where it would interfere with the determination of the iron. It can be recognized by the peculiar behavior of the iron solution on reduction with stannous chloride. The ferric iron is first reduced and when the liquid is almost colorless, the addition of more tin causes the color to deepen and take on more of a red tone due to the formation of platinous chloride.

The fusion must be conducted so as to reduce to a minimum the solvent action of the flux, that is, the amount of carbonate used must be as small as possible and the time of heating and the temperature must also be kept down. The best procedure is to heat the uncovered crucible directly over the blast flame, observing it all the time, and as soon as the mass is melted, shut off the gas. In this way the quantity of platinum dissolved is negligible. It might be added in this connection that platinum is also appreciably soluble in solutions of ferric chloride.

3. The titration of the iron in the solution of the silicious residue is conducted exactly as described for the main solution of the ore. Certain details, however, are omitted because of the small amount of iron present. No stannous chloride, for example, is used in dissolving the fusion and consequently no permanganate need be employed.

4. If an ore contains much organic matter, the weighed sample should be ignited at a red heat before solution in acids is attempted. (See also 41, 3.)

### VIII. PREPARATION OF A TENTH-NORMAL SODIUM THIOSULPHATE SOLUTION.

Sodium thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , is a reducing agent and in volumetric analysis is used almost exclusively in its reaction with free iodine. Iodine is readily and quantitatively set free from a solution of potassium iodide by oxidizing agents such as the permanganates, dichromates, chromates, iodates, bromates, peroxides, etc. The amount set free can be determined by titration with standard thiosulphate thus giving a general method for the valuation of such substances. Practice IX. is an illustration of one of these methods.

Sodium thiosulphate is decomposed by all acids, even by the weak carbonic acid, with the liberation of sulphur. Solutions of the salt in ordinary distilled water therefore become milky; but by using a carefully recrystallized product and water that has been boiled to expel carbon dioxide (110, 4) it is possible to prepare a solution that will stay clear. If time permits, however, it is far less labor and better in every way to use ordinary distilled water and allow the solution to clear by settling, a process needing, indeed, rather a long time, ten to fifteen days, but requiring no attention in the meanwhile. Prepared in this way the solution is stable and keeps perfectly for months. For this practice, then, about two liters should be made up at least ten days before it is to be standardized. The stock c. p. salt and ordinary distilled water may be used. The salt should be weighed to the nearest milligram, and in such quantity as to make the solution a trifle stronger than 0.1N. If the solution turns milky it must be given time to settle, after which 1500 cc. or so can be siphoned off into another bottle and standardized.

The reaction concerned in the use of thiosulphate is as follows:  $2\text{Na}_2\text{S}_2\text{O}_3 + 2\text{I} = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$ . The valence of the sulphur in  $\text{Na}_2\text{S}_2\text{O}_3$  is 2 and in  $\text{Na}_2\text{S}_4\text{O}_6$  it is 2.5. The valence change is therefore 0.5, and there being two sulphurs, there is a total change of 1, thus making the mol of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  the proper amount per liter for a normal solution. If students feel any intellectual difficulty over the appearance of the fractional valence, it can be avoided by saying that 2 sulphurs in  $\text{Na}_2\text{S}_2\text{O}_3$

have four valences and in  $\text{Na}_2\text{S}_4\text{O}_6$ , 2 sulphurs have 5 valences, the difference being 1. The query is frequently put as to why only two sulphurs in  $\text{Na}_2\text{S}_4\text{O}_6$  are considered. The answer to this is that the standard solution is made from the  $\text{Na}_2\text{S}_2\text{O}_3$  and not from the compound resulting from its reaction. Only the number of atomic weights in grams of sulphur in it are therefore to be considered and no further attention need be given to what becomes of them beyond noting the extent of the valence change.

In the standardization of the thiosulphate solution, advantage is taken of the reaction between dichromate of potassium and potassium iodide (107, 6). A measured amount of dichromate will liberate a definite amount of iodine which is then titrated with the thiosulphate using starch paste as indicator. The dichromate used may be either a weighed amount of the pure salt or a measured volume of standard solution (Practice VI).

A 10% solution of potassium iodide is used as the source of iodine. About 500 cc. should be prepared. On standing, such a solution frequently becomes yellow due to the liberation of a small amount of iodine. Before using, this yellow color can be discharged by adding a drop of thiosulphate solution to the contents of the stock bottle.

Another source of error is the presence of substances that liberate iodine when the solution is acidified. This point must be tested by adding 10 cc. of hydrochloric acid to 50 cc. of the iodide solution. If, after ten minutes, the liquid becomes yellow, starch-paste is added and the iodine titrated with the thiosulphate. The volume of thiosulphate so employed should then be subtracted from subsequent burette readings.

In some cases, however, there will be a continuous liberation of iodine which will be indicated by the reappearance of the blue color after the titration of the iodide solution as described above. This color can be discharged by more thiosulphate only to appear again in a short time varying from a few seconds to a number of minutes. When this happens, it is well, for a beginning student at any rate, to secure a new specimen of potassium iodide.

The liberation of a definite, small amount of iodine on acidifying a solution of potassium iodide was formerly thought to be due to the presence of potassium iodate,  $\text{KIO}_3$ . This is now denied and

the cause assigned to finely divided iron oxide which dissolves and liberates iodine.<sup>1</sup> The continuous, slow liberation of iodine is probably due to the presence of a catalytic agent which accelerates the action of the oxygen of the air. A trace of copper salt, for example, will set free a large amount of iodine from an acid solution of iodide. A complication likewise arises in the use of dichromate as a pure substance in liberating iodine for standardizing the thiosulphate. It also apparently acts as a catalytic agent and liberates more than the calculated quantity of iodine if used in solutions containing dissolved air. If, however, the air be expelled by bubbling an indifferent gas such as carbon dioxide through the liquid, this is not the case. It is of course difficult to prove experimentally that the greater amount of iodine liberated in the first instance is due to the acceleration by the dichromate of the action of the oxygen of the air on the iodide, because in the main reaction the dichromate also liberates iodine and is itself thereby destroyed. It can act as a catalyst then, only for the few seconds it exists as dichromate. The effect, however, is marked, amounting to about 0.3 cc. in a titration involving 25 cc. of 0.1N solution. In other words the iodine liberated by 25 cc. 0.1N dichromate in the presence of the oxygen of the air requires for its titration 25.3 cc. 0.1N thiosulphate. If the experiment be conducted so that air is excluded, 25 cc. of the thiosulphate will be used. The air may be excluded by bubbling carbon dioxide gas through the liquid or with less trouble by generating the gas directly in the solution as described below.

**Procedure.** Fifty cubic centimeters (measured in the cylindrical graduate) of the 10% potassium iodide solution are diluted in a large beaker to 800 cc. with distilled water and approximately 8 g. sodium carbonate added. Hydrochloric acid is now stirred into the solution in portions of a few cubic centimeters each till no further effervescence shows that all the carbonate is neutralized, when about 5 cc. in excess are added. The evolution of the large amount of carbon dioxide expels the dissolved air from the solution to which 50.00 cc. (pipette) of the 0.1N dichromate (Practice VI.) should now be added. This should be mixed through the liquid but with as little stirring as possible. The beaker is covered with a watch glass and allowed to stand for five minutes for the

<sup>1</sup> Andrews. J. Am. Chem. Soc. 31, 1035.

reaction between the dichromate and the iodide to complete itself. The cover is then removed, rinsed off and the solution titrated with the thiosulphate till the dark red color has given place to a light yellow. Starch paste (111, 5) is then added and the titration continued till the blue color gives place to a light green (Note 1). During the addition the stirring must be vigorous at the point where the liquid from the burette enters the solution in the beaker (Note 2).

Several titrations should be made and from the average of the closely agreeing results the normality of the thiosulphate solution should be calculated. (See 107, 6.)

**Notes.** 1. The end-point in the standardization of thiosulphate solutions as described above is peculiar and requires special mention in addition to the general matter of section 113, 2. When the starch paste is first added the liquid becomes dark green almost black in color. As the addition of thiosulphate continues, the green takes on more and more of a blue shade till finally the liquid is bright blue in color. This gradually loses in depth till the last trace of iodine disappears when it changes suddenly to the pale green of the chromium chloride. This succession of color changes is of great advantage as it shows the approach of the end-point. Beginners, however, often make the mistake of adding the thiosulphate too fast with the result that the blue stage is entirely missed.

In practicing with the end point as called for in 113, 2, the blank described on page 177 for the examination of the iodide can be used. The blue color is restored by the addition of a few drops of dichromate solution.

2. Success in this titration demands that the directions be followed closely. In the presence of the large excess of carbon dioxide the thiosulphate may be partially decomposed unless it is rapidly mixed with the liquid.

The large volume in which the titration is made is necessary to lower the partial pressure of the iodine and prevent loss by volatilization. The same effect but with less economy can be produced by adding more potassium iodide.

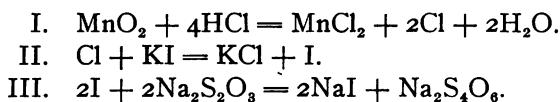
3. Other excellent methods for the standardization of thiosulphate solutions are the titration of a weighed amount of resublimed iodine and the use of potassium biiodate,  $KIO_3 \cdot HIO_3$ , for the

liberation of a definite amount of iodine from a solution of potassium iodide. It is interesting to note that this latter salt sets free the same amount of iodine whether used in the presence or absence of the oxygen of the air. Students desiring extra work will do well to look up the details of these methods.

## IX. DETERMINATION OF THE TOTAL OXIDIZING POWER OF PYROLUSITE.

The mineral pyrolusite is the naturally occurring manganese dioxide,  $MnO_2$ . It is not pure but contains small amounts of other reducible oxides together with some silicious matter. The titration of such material gives the sum of all its reducible constituents, but since in its industrial application, only the total oxidizing power is wanted, no attempt is made to separate them. Just as in the case of soda ash (page 165), the titration of the mixture is made and the result stated in terms of the most important constituent, in this case the  $MnO_2$ .

According to the method as given below, the sample is first boiled in a flask with concentrated hydrochloric acid whereby the oxides of manganese are reduced and an equivalent amount of chlorine set free. This chlorine is conducted into a solution of potassium iodide where it liberates iodine, which is then titrated with standard thiosulphate solution. The reactions involved are as follows:



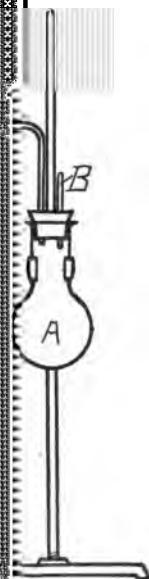
The relation between the thiosulphate and the manganese dioxide is readily worked out by observing that  $2Na_2S_2O_3 = 2I = 2Cl = MnO_2$ . Hence,  $2Na_2S_2O_3 = MnO_2$ . If, however, the thiosulphate solution is on the normal basis, the relation can be found more simply. (See 107.) One cubic centimeter of a 0.1N  $Na_2S_2O_3$  will correspond to 1 cc. of a 0.1N  $MnO_2$ . The manganese in  $MnO_2$  (reaction I. above) changes 2 in valence, therefore the mol divided by 2 gives the amount per liter for normal. (See 107, 7 for factor weights.)

A new point in manipulation is brought out in this method, namely, the separation and quantitative handling of a gas. This involves a special apparatus the construction of which should receive as much study as any part of the process. A quantitative apparatus should be as simple as possible consistent with its purpose; should be so designed as to make its operation easy and sure

### *Technical Analysis.*

raftsman-like manner. Students should consider that any awkward tubing will serve. In this sketch should be reviewed.

adapted to the requirements of round bottom flask of 60 to 70 ml. containing the sample. The evolved gas passes through tube C to the bottom of the iodide solution. The tube D through which cold water is kept



from becoming too hot and occurring. A very size test tube containing a small amount of iodine escaping from D. It serves as a guard tube to prevent iodine from entering G, the tube E being fused at the point where it enters G. The flask A is attached directly to the tube D and stands. This gives the whole apparatus a compact and convenient form to manipulate. The flow

of water through the vessel G is easily managed by siphoning out with a piece of rubber tubing or, if a large beaker is used, it can be inclined towards the side with the lip and the water allowed to overflow into the sink.

**Procedure.** About 50 cc. of 10% potassium iodide solution diluted to 75 cc. are put into the large tube D and 3 to 4 cc. into the small tube F. The apparatus, with the exception of the evolution flask A, is then connected and the stream of water for cooling started. A factor weight (107, 7) or about 0.5 g. sample is next weighed, placed in A (37, 1), 20 cc. of strong hydrochloric acid added, and the flask immediately connected with the rest of the apparatus. The action of the acid on the pyrolusite is slow in the cold so there is no danger of loss of chlorine if reasonable promptness is used. As soon as the apparatus is properly connected the contents of the flask should be heated with a small, free flame, holding the burner in the hand. The heating must be so regulated that a too rapid evolution of chlorine does not take place at first, though after some minutes the liquid in the flask should be boiled rapidly. This boiling must be continued for a minute or two till the steam and hydrochloric acid have driven over all the chlorine (Note 2). The burner is then set under the flask and the plug B, which must not fit too tightly, is withdrawn. This introduces air and prevents the liquid in D from being drawn back into the flask.

Before beginning an analysis the student is recommended to try the experiment of boiling hydrochloric acid alone in the flask, the tube D being charged with water. A little practice may show the weak points in his manipulation without occasioning the loss of a determination.

When the plug B has been removed, the apparatus is disconnected, care being taken to rinse out any iodine that may be retained in the tubes C and E. The solutions in F and D are poured into a large beaker containing 300 to 400 cc. of water for dilution and are titrated (Note 3) at once with standard thiosulphate (Practice VIII.).

From the result of the titration the percentage of  $MnO_2$  is calculated and reported as, Total Oxidizing Power in Terms of  $MnO_2$ .

**Notes.** 1. Paraffined corks are to be preferred to rubber stoppers on account of the action of chlorine on rubber, though fairly good results can be obtained with the latter if they are previously boiled in caustic soda solution to remove sulphur. Beginners should, however, use corks not only for the reason that results are likely to be more uniform but also for the practice in setting up a quantitative apparatus with cork connections.

In the use of corks in apparatus building the following points should be observed: (1) Care must be used in selecting one of good quality and of the right size. It must be noted that rolling or softening reduces the size and increases the elasticity to such an extent that one apparently too large must be chosen. A good rule is to start with one the smaller end of which barely enters the aperture to be closed. (2) Before the cork is bored it must be softened in a corkpress or by rolling it under a piece of board, for example, the base of the filter stand. If this latter method is employed some attention should be given to the cleanness of the desk and board. (3) The size of the cork borer must be adapted to the tube intended for the hole. A good workman will first make a trial boring through a piece of card board or scrap cork and if, as frequently happens, a borer exactly suited to the tube is not at hand, the size smaller is used and the hole then enlarged with a round file. If necessary the borer should be sharpened which, if a special sharpener is not available, can be done by filing the cutting edge. (4) In the actual operation of boring, the cork is held in the left hand and the borer in the right. A straight boring can be achieved by rotating the cork through a quarter turn at each twist of the borer as it is forced through. When more than one hole is to be bored, the start should be made at the smaller end. If but one hole is to be put through the center, the boring should be made from both ends. The hole is finally cleaned out with a round file and enlarged, if need be, to the proper size.

The paraffining is done simply by immersing the cork in melted paraffine fifteen or twenty seconds. It should not be left in too long or so much will be absorbed that the elasticity of the cork will be impaired.

2. The trick of knowing when all gas or air has been expelled from a liquid can be learned from this practice. It will be observed that after boiling a few minutes, bubbles no longer reach

the top of the iodide solution and a sharp rattling sound is produced where the steam from the evolution flask passes into the liquid. This rattling sound marks the expulsion of all gas. On boiling a minute or so after its appearance the chlorine may be considered expelled.

3. The titration of the iodine set free by chlorine is the same as described in Practice VIII. Starch paste (III, 5) is added when the red color has almost disappeared and the addition of thiosulphate then continued till the blue disappears. The end-point will not be complicated in this case by the green of the chromium salts.

Since the solution in the tube D is rather concentrated, it is poured into a large volume of cold water to prevent loss of iodine.

## X. DETERMINATION OF PHOSPHORUS.

The so-called molybdate-magnesia method for the determination of phosphorus is considered the most accurate and is the one employed in the following practice work. It consists of three steps: (1) Solution of the sample and oxidation of the phosphorus, if necessary, to phosphoric acid. (2) Separation of the phosphorus from other acids and bases by precipitation as ammonium phosphomolybdate. (3) Solution of this precipitate and reprecipitation of the phosphorus as magnesium ammonium phosphate which is then ignited and weighed as magnesium pyrophosphate. With appropriate modifications for getting the sample into solution the method is of general application to all sorts of material whether of high or of low content in phosphorus.

The required work of this practice consists in making the special reagents as needed, and in the determination of phosphorus in two samples, one in which the percentage is quite high, as in rock phosphate or fertilizer, and one in which it amounts to only a few tenths of one per cent. or less, as in ores, pig irons and steels.

**Special Reagents.** 1. Molybdate Solution. For 500 cc. of finished solution, 25 g. of molybdic acid,  $\text{MoO}_3$ , are dissolved in about 100 cc. of ammonia water (sp. gr. 0.96, 9.9%  $\text{NH}_3$ ). If solution appears slow, warming and the addition of a few more cubic centimeters of strong ammonia will hasten it. This solution is finally cooled and poured in small portions at a time, with intermediate shaking, into about 300 cc. of dilute nitric acid (sp. gr. 1.20, 32.5%  $\text{HNO}_3$ ). The whole is then diluted to 500 cc. One cubic centimeter of this solution will precipitate about 0.001 g. of phosphorus.

2. Magnesia Mixture. 250 cc. should be prepared. 3 g. roughly weighed, of calcined magnesia,  $\text{MgO}$ , are dissolved in dilute hydrochloric acid taking care to use no more than is necessary. An excess of magnesia is then added and the mixture heated. Any iron, alumina or phosphates that may be present will be precipitated and should be removed by filtration. About 35 g. ammonium chloride and 25 cc. of strong ammonia (sp.gr. 0.9) are then added

and the liquid diluted to 250 cc. If, after a time, a slight precipitate settles out it may be filtered off or, if care be used in pipetting from the bottle, it may be allowed to remain. One cubic centimeter of this solution is equivalent to about 0.016 g.  $P_2O_5$ .

3. Ammonium Nitrate Solution. This is used for washing the ammonium phospho-molybdate and should be from 5 to 10% in strength. It can be made by dissolving the appropriate amount of salt and acidifying the solution with nitric acid, using about 1 cc. per liter in excess. It can also be made conveniently by diluting the calculated volume of strong nitric acid (sp. gr. 1.42 and 69%  $HNO_3$ ), adding ammonia till alkaline to litmus paper and then nitric acid slowly till again acid, using the excess as given above. Dilution to the requisite volume is finally made and as soon as cool it is ready for use.

4. Ammonia Water. This is used for washing the magnesium ammonium phosphate and for dissolving the ammonium phospho-molybdate. It is the same as that employed in limestone analysis. (See p. 155, Note 10.)

5. Magnesium Nitrate Solution. For 100 cc. 16 g., roughly weighed, of calcined magnesia are dissolved in a small amount of dilute nitric acid. An excess of magnesia is then added and after heating for a few minutes the solution is filtered and diluted to 100 cc.

**Solution of the Sample.** The following general points are observed: (1) The phosphorus must be present as phosphoric acid,  $H_3PO_4$ , or one of its salts, in order to be precipitated by molybdic acid. Other forms are brought to this state by strong oxidizing agents, therefore in dissolving the sample, the conditions should be oxidizing. (2) Soluble organic matter if present must be destroyed as otherwise it would reduce the molybdic acid. This is also accomplished by the use of strong oxidizing agents. (3) In the case of ores or rock material, the excess of silicic acid must be removed as it is partially precipitated by molybdic acid. This is accomplished in the usual way by evaporating the acid solution to dryness. Two evaporation are unnecessary as the small amount left after the first one is negligible.

The application of the above general principles should be noted in the special cases described below. Ores or rock material in general may be dissolved in hydrochloric or nitric acids, or in aqua

regia, any insoluble silicious matter being fused with sodium carbonate (41, 4) and the fusion dissolved in acid. The combined acid solutions are then evaporated to dehydrate the silicic acid which is filtered off. (See page 152, Note 1.) Simple ignition (41, 3) may also be employed to render rock material soluble in acids.

As a general rule the insoluble silicious matter from an ore or rock does not retain phosphorus. There is, however, no way of knowing this in any given case except by trying it. One such residue ought to be fused and tested separately. If found to contain more than a trace of phosphorus its solution is combined with the main one. If no phosphorus is found the insoluble residues in the case of subsequent determinations on that lot may be discarded. For the special procedure when titanium is present, see below.

Metals, as for example iron and steel, must be dissolved in nitric acid or aqua regia. If hydrochloric acid, or in general a non-oxidizing solvent were used, some phosphorus would be lost, owing to the formation of phosphine gas by the action of the acid on phosphides. The nitric acid solution is evaporated to dryness and the residue strongly heated on the hot plate or over a free flame to insure the destruction of carbon compounds and the complete oxidation of the phosphorus.

When the sample contains much organic matter as is the case with animal and vegetable products, a special procedure must be used in destroying it. Simple ignition, while efficient, is not admissible for in some cases a loss of phosphorus may occur. Either a wet process of oxidation must be used or the ignition be made in the presence of an oxidizing agent. Examples are given below under the procedure for fertilizers.

**General Procedure.** While details vary according to the nature of the material under examination certain points are of general application and will be discussed here.

Precipitation with Molybdate Solution. This is the first step after the solution of the sample and effects a separation of the phosphorus from the other substances in solution. The precipitate produced has the formula  $(\text{NH}_4)_3\text{MoO}_4\text{PO}_4$  and, to avoid the repetition of the long name, ammonium phospho-molybdate, it is generally called simply the yellow precipitate. While there are methods based upon the weighing of this precipitate, its composition

is so susceptible to slight changes in conditions, that they have not been generally accepted. (See 47.)

The conditions favorable to its rapid precipitation in a form easily filtered are the absence of free acids excepting a small amount of nitric, the presence of a large excess of ammonium nitrate and a warm though not too hot solution. These conditions are readily and easily obtained by adding to the solution of the sample, irrespective of the acid employed, 8 to 10 cc. of concentrated nitric acid, then ammonia till slightly alkaline, and finally nitric acid again till the liquid is distinctly acid. This procedure results in the formation of the requisite quantity of ammonium nitrate and the heat of the reaction brings about the desired rise in temperature. As a rule the solution contains sufficient iron, aluminum and calcium to occasion a copious precipitate with ammonium hydroxide. Its appearance can therefore be taken as a sign of alkalinity. Nitric acid is then added till the precipitate redissolves. In case such a precipitate fails to appear, a little piece of litmus paper may be put into the liquid.

Molybdate reagent is added at once to the warm solution in a slow stream from a pipette, accompanied by vigorous stirring. This reagent is always used in large excess, the volume ranging from 40 cc. in the case of ores, pig iron and steels, to 75 to 100 cc. in the case of phosphate rock and some fertilizers. The beaker should be set aside for at least thirty minutes, or for an hour or more in the case of low percentages of phosphorus, after which the clear, supernatant liquid may be tested for completeness of precipitation by pipetting out about 5 cc. and adding an equal volume of molybdate. The mixture should remain clear on warming and letting stand ten minutes. Sometimes a white cloudiness appears which does not look like the yellow precipitate, in which event the test should be repeated. In case a yellow precipitate forms, the test portion is returned to the main solution and 15 to 20 cc. more molybdate reagent added. This may be poured in rapidly but the contents of the beaker should be stirred and, after settling clear, another test is made.

The precipitate is finally filtered and washed with ammonium nitrate solution acidified with nitric acid as described above. The beaker in which the precipitation took place is merely rinsed out as it is subsequently placed under the funnel when the precipitate

is dissolved (see below). The washings may be tested for chlorine if much hydrochloric acid had been employed in the original solution, or if much iron and calcium are present, ammonia and ammonium oxalate may be used. If sulphuric acid was used as a solvent, barium chloride may be used to test the washings. Students should not forget to make a blank test on the washing solution alone.

Precipitation with Magnesia Mixture. After the filtration and washing of the yellow precipitate, it is dissolved through the filter into the original beaker with dilute ammonia, for which purpose the solution described above under special reagents may be used. It is most conveniently handled, both for this purpose and for washing the magnesium ammonium phosphate, if contained in a wash bottle. In dissolving the yellow precipitate the filter should be washed down from the top and if a large amount of precipitate is present the stream may occasionally be directed into the mass to churn it up. The filter should be washed several times after the complete disappearance of the precipitate. One or two washings are then made with water to remove the excess of ammonia after which moderately strong hydrochloric acid is dropped around the edge of the paper to dissolve traces of ferric or other hydroxides which might retain phosphorus. If yellow stains appear on the filter following the treatment with acid it shows that all of the yellow precipitate had not been removed and accordingly, after washing once or twice with water, more ammonia must be used. If no stains appear the acid is washed out with water. When this acid liquid reaches the solution below a partial precipitation may be produced but this is disregarded. Finally, the sides of the beaker and the stirring rod are washed down with dilute ammonia to dissolve any adhering precipitate after which preparation is made for the second precipitation as magnesium ammonium phosphate (Note 1).

The conditions favorable to the precipitation with magnesia mixture are the presence of a small amount of ammonium chloride, ammonia in slight excess and a cold solution. The production of the ammonium chloride and regulation of the excess of ammonia are managed by adding hydrochloric acid slowly with stirring till the yellow precipitate which reappears as the solution becomes acid, just fails to dissolve. Ammonia is then added till this pre-

cipitate disappears. In case the original ammoniacal solution of the yellow precipitate had been cloudy, especially if brown, thus indicating iron, 6 to 7 drops of a saturated solution of citric acid are added after the addition of the hydrochloric acid above. This in no wise interferes with the subsequent precipitation of the phosphorus but prevents the precipitation of iron and alumina by the ammonia.

Attention is now given to the dilution. With care the volume of liquid at this point should range from 40 to 50 cc., in the case of very small amounts of phosphorus, to about 100 cc. in the case of the larger amounts as found in phosphate rocks. An experienced chemist could judge from the bulk of the yellow precipitate as to the amount present. For the student, however, the following suggestions must suffice: If a 9 cm. filter is employed and it was half-full of precipitate, the solution should be diluted to 150 to 175 cc. From this the volume grades down till, for the small amounts of phosphorus in ores, etc., no dilution is necessary, the beginner doing well if the solution of the yellow precipitate is not already too large.

After the proper dilution, the solution is ready for the addition of magnesia mixture, which must be made drop by drop with constant stirring. It is most conveniently managed from a burette. About one-fourth more than is theoretically required for the precipitation of the phosphorus present should be used. In the case of very small amounts, however, as in ores, etc., this proportion may be exceeded. In the estimation of the volume of precipitant the chemist of experience is again guided by the bulk of the yellow precipitate. For beginners the following rules may be used till a preliminary determination gives more accurate information. If a 9 cm. filter was half-full of yellow precipitate, 15 to 18 cc. of magnesia mixture should be used. From this the volume to be added grades down to 2 to 3 cc. when very little phosphorus is present. If the precipitate, which should be crystalline, is slow in appearing, more ammonia may be added. In any event at the conclusion of the precipitation the solution should smell strongly of ammonia. The precipitate may be filtered after four hours though in the case of very small amounts it is better to wait longer. It is not dissolved and reprecipitated and is not ignited over the blast lamp (Note 2), but in all other respects its filtration, washing and

ignition are conducted as described for the same precipitate on page 152. The ignition is made over the Bunsen burner, its full heat being maintained for ten or fifteen minutes.

In this practice students should use the Gooch crucible as described in section 55.

**Procedure with High Percentage of Phosphorus.**<sup>1</sup> The fertilizer industry makes the most frequent calls for the determination of phosphorus in material high in percentage of that element. Results are as a rule stated in terms of  $P_2O_5$ , the values ranging from 1 or 2% in low grade fertilizers to 30% or more in good specimens of the untreated phosphate rock.

Owing to the bulk of the yellow precipitate and the costliness of molybdic acid, no more than 0.5 g. or at most a factor weight (37, 6) of sample ( $P_2O_5$  in  $Mg_2P_2O_7$ ), should be taken for an analysis. Indeed, good results can be obtained with half a factor weight.

Methods of solution vary according to the character of the material, the necessary details being as follows:

(1) For Phosphate Rock. This is the naturally occurring, impure tri-calcium phosphate from which the so-called rock-phosphate of the fertilizer industry is prepared by treating it with sulphuric acid. It is a perfectly stable material which can be ground to a fine powder and is therefore easily sampled.

About 0.5 g. or a factor weight of the finely ground rock is weighed into a casserole and treated with 30 cc. of hydrochloric acid plus 1 cc. of nitric acid. A watch glass is now put on and the mixture boiled to dryness over a free flame, the casserole being held in the hand and kept rotating during the operation (Note 3). The dry residue is heated for a minute or so after all liquid has been driven out, after which it is cooled, treated with about 5 cc. of hydrochloric acid, warmed, diluted to 25 or 30 cc., filtered and washed with hot water till the washings no longer taste sour.

The solution is now ready for the addition of nitric acid, ammonia, etc., as described above for the precipitation of the yellow precipitate. At least 75 cc. of molybdate solution should be used.

The yellow precipitate when obtained is filtered, washed, dissolved and the phosphorus precipitated with magnesia mixture as described above.

<sup>1</sup> Adapted from the publications of the Official Agricultural Chemists.

(2) For Fertilizers. Most commercial fertilizers consist of various mixtures of organic and inorganic material, much of which can not be finely pulverized. The samples are therefore coarse and the plan given in 37, 4 should be used. Four or five times the factor weight is dissolved and diluted so that no more than 50 cc. need be taken to give the desired amount for the analysis.

Two methods of solution are given below from which the student may make his choice. Both are of general application and equally efficient in the safe destruction of organic matter.

(a) The weighed sample is placed in a moderately large porcelain crucible or small evaporating dish and about 6 cc. of the magnesium nitrate solution described above added. If the nitrate solution does not readily wet the sample owing to the presence of grease, a little alcohol should be added. The mass is then stirred to insure an intimate mixture, the stirring rod being finally rinsed off with the least possible quantity of water and the vessel set on the water bath or steam box till the liquid is entirely evaporated. The residue is then cautiously heated with a Bunsen burner, finally to redness, till the organic matter is destroyed as shown by the disappearance of all black (Note 4). After cooling, the mass is transferred as follows to the graduated flask in which the solution is to be diluted: A funnel is set in the flask and the contents of the dish moistened with a little water to prevent loss through dusting. As much as possible of the material is now scraped from the dish into the funnel by means of a stirring rod or spatula. The dish is then rinsed out with concentrated hydrochloric acid followed by a little water from the wash bottle. During these operations it must be held over the funnel. The underside of the lip must also be rinsed off. In this way the contents of the dish are transferred to the flask with the use of as little water as possible. If need be, more hydrochloric acid to make the volume up to 50 cc. is added and the mixture boiled gently for 30 minutes (Note 5). At the end of this period, the liquid is cooled to room temperature, diluted to the mark and mixed (98, 4). Two procedures are now open; the solution may be allowed to settle clear and the proper aliquot part pipetted out, or some of it may be filtered through a dry filter and the portion pipetted from the clear filtrate (Note 6).

The aliquot part of the solution taken is placed in a beaker,

treated with nitric acid, ammonia, etc., and finally precipitated with molybdate solution, the general procedure being followed from this point.

- (b) The weighed sample is digested in a Kjeldahl digestion flask with sulphuric acid and potassium sulphate as described under the determination of nitrogen page 213. At the conclusion of the digestion the acid solution is diluted, (see page 214) and transferred to the graduated flask where it is filled to the mark and mixed (98, 4). An aliquot part is then pipetted into a beaker and from this point the general procedure above followed. Owing to the presence of the sulphuric acid, about 10 cc. of nitric acid should be used to insure a greater portion of ammonium nitrate. (See also General Note 1.)

**Procedure with Low Percentage of Phosphorus.** The classification according to percentage of phosphorus is an artificial one, as the only modification of the general procedure dependent upon it is the variation in the amount of sample used in the analysis. It is a general rule that when only a few tenths or hundredths of one per cent. are to be found, 2 to 5 g. of sample or an equivalent multiple of the factor weight should be taken. Otherwise the amount of precipitate obtained is so small that the inevitable errors due to impurities and the like become large percentage errors. (See also section 40.) Apart from this the procedure is determined by the chemical and physical character of the material. It happens, however, that the percentage of phosphorus is, as a rule, low in metallurgical materials and products and consequently the classification as given above coincides roughly with the nature of the substances examined. In the metallurgical industries results are stated in terms of phosphorus rather than as the anhydride,  $P_2O_5$ .

- (1) For Iron Ores. From 2 to 5 g. or from 10 to 20 times the factor weight ( $P$  in  $Mg_2P_2O_7$ ) are finely ground in an agate mortar and treated in a covered casserole with from 40 to 80 cc. of concentrated hydrochloric acid, the larger volume of acid being used with the larger amount of sample. The mixture is boiled gently for 15 to 20 minutes to dissolve the ore after which the heat is increased and the solution taken rapidly to dryness (Note 3). When the liquid is all expelled the heating is continued — with the cover glass on — by rotating the casserole over a free flame

or leaving it stand on the hot plate heated from below, till the mass is baked dry and hard. There is no danger of its becoming too hot.

After cooling, the residue is treated with 30 to 50 cc. of hydrochloric acid, the watch glass again put on and the mixture boiled down to 15 to 20 cc. Water is then added to bring the volume up to 55 to 60 cc. and, after boiling again for a minute or so, the solution is ready to filter from the insoluble silicious material. This is washed with hot water till the washings no longer taste sour.

At least one insoluble residue in the case of ores should be ignited and fused (41, 4). The fusion is dissolved in dilute hydrochloric acid, the silica removed by one evaporation (page 152, Note 1) and the solution tested for phosphorus according to the general procedure above. The residue may also be assumed to contain phosphorus, in which case it is not tested separately but, after fusion, the melt is dissolved by means of the main solution of the ore, using more hydrochloric acid if necessary. (A similar procedure described under limestone analysis, page 147, should be reviewed.) The combined solutions are then evaporated (Note 3) and the silicic acid separated as described on page 147.

The hydrochloric acid solution thus obtained is ready for the addition of 10 cc. nitric acid, ammonia, etc., as described in the general procedure above. At least 40 to 50 cc. of molybdate solution should be used notwithstanding the small amount of phosphorus present.

The yellow precipitate is finally filtered, washed, dissolved in ammonia and the phosphorus precipitated with magnesia mixture in the usual way.

(2) For Pig Iron and Steel. From 2 to 5 g. or the equivalent multiple of the factor weight is dissolved in a casserole in 30 to 70 cc. of moderately strong nitric acid, care being taken to prevent loss due to the violent action of the acid on the metal. After solution is complete, the liquid is evaporated to dryness (Note 3) and the residue thoroughly baked as described above for ores. More attention, however, should be paid to this point than in the case of ores as the complete oxidation of the phosphorus depends upon it. The heating must last an hour if done on the hot plate or for thirty minutes if done by rotating the casserole over a free flame.

After the mass is cool, it is treated with 15 to 30 cc. of concentrated hydrochloric acid, and again evaporated to dryness (Note 8). The residue need not, however, be heated more than enough to dry it thoroughly. Hydrochloric acid is then added for the second time and the casserole heated — with watch glass on — till all the iron oxide is dissolved, after which 30 to 40 cc. of water are added and the mixture boiled for several minutes. The cover is then rinsed off and the solution filtered from the insoluble silicic acid. From this point the procedure is the same as for ores.

**Modification When Titanium is Present.** The effect of titanium is three-fold: (1) It causes phosphorus to be retained in the silicious residue or, if the residue be fused and treated in the usual way to remove silica, the silicic acid will contain phosphorus and titanium. (2) Some titanium will go into solution and when the yellow precipitate is dissolved, a residue containing phosphorus will remain on the filter. (3) It negatively catalyzes the rate of precipitation of the yellow precipitate, making it necessary to use larger amounts of molybdate reagent and allow more time for the completion of the precipitation.

The presence of titanium is indicated by a tendency to "run through" when the insoluble silicious residue of the sample is washed. The acid solution of the sample may also become turbid on dilution owing to the precipitation of titanium hydroxide produced by hydrolysis.

If the above signs indicate the possible presence of titanium the washing of the silicious residue is nevertheless continued and the residue itself retained for the special treatment below. No regard also is given to the precipitate produced by the addition of water to the acid liquid as the phosphorus retained by it is recovered in the subsequent treatment of the filter through which the yellow precipitate is dissolved. The usual procedure is followed as far as the solution of the yellow precipitate, when the paper through which it was dissolved and also the one containing the insoluble silicious matter are ignited in a platinum crucible. The residue now free from carbonaceous matter is then fused with sodium carbonate (41, 4), and the resulting mass boiled with a little water till thoroughly disintegrated, when the solution is filtered. Sodium titanate being insoluble remains on the filter and the phosphorus passes through as phosphate. The filtrate is then

acidified, evaporated to dryness to dehydrate the silicic acid, the residue taken up with dilute acid and filtered. The phosphorus is now precipitated in this acid liquid in the usual way and the yellow precipitate obtained dissolved and combined with the main portion. One precipitation with magnesia mixture will then be sufficient.

Owing to the small amount of phosphorus present in the residue as treated above, care should be used to keep the volume of the final solution low. If this is done 25 cc. of molybdate reagent will effect complete precipitation.

**Modification when Arsenic is Present.** Arsenic behaves towards molybdic acid and magnesia mixture in practically the same way as phosphorus. If present, therefore, it precipitates and causes high results. Its precipitation with molybdic acid is, however, so strongly affected by the temperature that when small amounts are present and the solution is cooled to 20 degrees or less before adding the molybdate reagent, the yellow precipitate will be practically free from it. It is nevertheless safer to remove it with hydrogen sulphide.

The sample is dissolved in the usual manner, any nitric acid being expelled with hydrochloric acid. The addition of hydrogen sulphide at this point, however, with no reference to the large amount of ferric salts present, would result in the precipitation of a quantity of sulphur. The problem then, is first to reduce the iron by another and less objectionable method before using the hydrogen sulphide. This can be accomplished by sulphur dioxide generated in the solution by the action of acid on sodium sulphite.

The acid solution of the sample is first nearly neutralized with sodium carbonate, after which strong solution of sodium sulphite is added in small portions accompanied by the addition of hydrochloric acid from time to time to preserve the acidity of the liquid. The mixture is then heated to boiling, more acid being used if a precipitate forms. The end of the reduction of the ferric salts is shown by the solution becoming colorless. Continued warming and the addition of more sulphite are sometimes necessary. When all the iron is reduced, 10 to 12 cc. of hydrochloric acid are added and the solution boiled till the sulphur dioxide is expelled. Hydrogen sulphide is then passed into the hot liquid which precipitates the arsenic and other metals of that group that may be

present. The precipitate is filtered and washed with dilute hydrogen sulphide water. The filtrate is boiled to expel the excess of  $H_2S$  and the iron oxidized by the addition of nitric acid. (See top of page 140.) The solution is now ready for the precipitation with molybdate reagent.

The procedures in the presence of titanium and arsenic are given, not because the ores that are used in this practice work are likely to contain these elements, but because they illustrate so well difficulties that may arise and the complex operations necessary to overcome them. Their study as examples of special cases is recommended.

**Notes.** 1. In preparing for the precipitation with magnesia mixture, attention should be given to the cleanness of the apparatus as well as to the chemical operations. The outside of the beaker and the cover glass should be rinsed with distilled water and wiped dry. In the case of low-phosphorus samples the beaker in which the yellow precipitate is thrown down is usually too large for the precipitation with magnesia mixture and a smaller one should accordingly be provided for receiving the ammoniacal solution. If this is to be done the usual procedure is followed to the point where the yellow precipitate is dissolved, when the smaller beaker is placed under the funnel. The stirring rod and the sides of the original beaker are then rinsed down with ammonia and the liquid poured through the filter. In this way the precipitate adhering to the glass is removed and the main portion on the filter is dissolved with the least possible volume of liquid.

2. The precipitate obtained with magnesia mixture is rarely pure magnesium ammonium phosphate and according to Neubauer<sup>1</sup>, loses  $P_2O_5$  on blasting. Neubauer has studied this loss and furnishes a table of corrections. If, however, the precipitate is not blasted, compensating errors result that give a value very nearly agreeing with the formula  $Mg_2P_2O_7$ .

3. The details of taking to dryness the solution of rock or ore in which phosphorus is to be determined will vary with conditions. Section 64 should be reviewed. If the sample is dissolved just before noon or in the evening, it is economy of time to place the vessel on the steam box or water bath for the evapora-

<sup>1</sup>Z. Anorg. Chem. 2, 45 and 4, 251.

tion. If, on the other hand, the work is to be pushed, the plan given in 64, 2, second paragraph, can be used. With a little care even the solution of a rock high in phosphorus can be boiled down in a covered casserole without loss.

4. The ignition of the residue from the evaporation with magnesium nitrate solution sometimes presents difficulty. Certain materials like tankage and bones swell up on being heated and burn with great rapidity. These must be handled with great care to prevent loss. Under no circumstances is it permissible at first to set the crucible over a flame and leave it without attention. The heating should be done with the burner in the hand till all danger of spattering or too rapid combustion is over. An excellent trick of manipulation to employ while the residue is still moist, is to turn the Bunsen flame directly into the crucible.

5. A beginning student will at first hesitate over boiling a solution in a graduated flask though as a matter of fact such a flask is no more likely to break than another. An alternate procedure is to boil the sample in a beaker or other vessel and subsequently transfer it to a graduated flask for dilution.

6. A dry filter must be used in order not to dilute the solution. Another procedure is to start with a wet filter but reject the first 25 to 30 cc. that run through. This is equivalent to rinsing the paper. The point referred to in 48, 8 can be disregarded in this connection unless very refined work is attempted.

7. When a nitric acid solution containing silicic acid is evaporated to dryness the insoluble residue, as a rule, filters slowly, and it is therefore a time-saving device to evaporate a second time with hydrochloric acid.

**General Note.** Fertilizer analysis affords an excellent example of how time and labor can be saved in commercial work by having a well thought out plan. Many samples require the determination of both phosphoric acid and ammonia and it is evident that if the Kjeldahl method of digestion is employed, both can be made from the same solution thus sparing the weighing and dissolving of a second sample. Still further labor can be saved by the use of factor weights. In the author's laboratory, for example, the following has been employed: Five times the factor weight of sample, 3.1880 g., were digested with sulphuric acid and potassium sulphate and the solution diluted to 500 cc. This was al-

lowed to settle clear and 50 cc., representing 0.3188 g., were used for the  $P_2O_5$  determination. The weight of  $Mg_2P_2O_7$  obtained, when multiplied by 2, gave directly the percentage of  $P_2O_5$ . For the ammonia distillation, 100 cc. representing 0.6376 g. were used. This amount has no simple relation to any  $NH_3$  factor but in volumetric work such a situation is easily managed by making the standard solution fit the amount of sample. In this case, for instance, the standard ammonia (see page 209) was made of such strength that 1 cc. = 0.003188 g.  $NH_3$  or 0.5% of 0.6376 g., the amount used. The number of cubic centimeters equivalent to the  $NH_3$  in the sample is then divided by 2 to give the percentage.

**XI. DETERMINATION OF SODIUM AND POTASSIUM.**

The problem presented in the determination of sodium and potassium in a substance insoluble in acids is somewhat complicated by the fact that the ordinary method of fusion with sodium carbonate is inadmissible. Fluxes such as PbO and B<sub>2</sub>O<sub>3</sub>, which do not contain sodium and potassium can be used but the subsequent separations are complicated and lead to many chances of error. The same is true of the method of decomposition by means of hydrofluoric and sulphuric acids. A third plan depends on a somewhat different principle. The insoluble material is heated with its own weight of ammonium chloride and a large excess of calcium carbonate. The mixture does not fuse but sinters together into a dry mass in which the sodium and potassium are in a form completely soluble in water. This plan known from the name of the inventor as the J. Lawrence Smith method is the one in common use and will therefore be described in detail.

On heating together the rock powder, ammonium chloride and calcium carbonate, the insoluble silicates containing the sodium and potassium, for example feldspars, are decomposed with the formation of the chlorides of these metals and calcium silicate. Oxides, carbonates and soluble silicates of the other bases are formed, together with a large amount of calcium oxide from the ignition of the excess of calcium carbonate. On treating this dry mass with water the alkaline chlorides go into solution and the calcium hydroxide formed precipitates the soluble salts of the iron group and also those of magnesium. On filtering this mass the filtrate contains nothing but the alkalis and the excess of lime water. The latter is removed by precipitation with the volatile reagent ammonium carbonate which is in its turn expelled by evaporation and ignition of the residue. From this residue of sodium and potassium chlorides the potassium is precipitated with platinum chloride and the sodium determined by difference (Note 1). The details of the procedure are as follows:

**Procedure.** 1. Preparation of Sample and Charging the Crucible (Note 2). About 0.5 g. of sample is taken. This should be very finely ground in an agate mortar (37, 3) before weighing. An approximately equal amount of ammonium chloride—a few

milligrams more rather than less—is then weighed and the two intimately mixed by grinding together in the mortar, care being used to avoid loss. About 4 g., or eight times the weight of the sample, of calcium carbonate (Note 2) are next weighed and a small portion, 0.5 g., placed in the bottom of the platinum crucible in which the decomposition is to take place. Another small portion is reserved for covering the top of the mixture after it is in the crucible. The remaining and larger portion is then intimately mixed, by further grinding, with the sample and the ammonium chloride. Much depends on this, therefore the grinding should occupy four or five minutes and be done in such a way as to insure thorough mixing. The transfer to the crucible is made by first pouring the material onto a piece of glazed paper. Anything adhering to the end of the pestle should be brushed off as well as the last traces left in the mortar. The reserved portion of the calcium carbonate may be ground lightly and poured by way of the paper into the crucible. It serves to rinse them both. Mortar, pestle and paper are again brushed off and the mixture settled by gentle tapping (Note 3).

2. Method of Heating. The closely covered crucible is supported in a triangle so that the bottom is about one inch above a low flame. It is heated in this way for ten or fifteen minutes or until no further smell of ammonia can be detected, when the flame may be turned up so that the lower half or less of the crucible becomes red hot. This is continued for about an hour when the decomposition may be considered complete and the crucible allowed to cool (Note 4).

3. Treatment after Heating. The mass in the crucible will be found greatly shrunk in size. It consists largely of lime, CaO, which is to be slaked by the addition of water, a few drops at a time, until the whole is softened and may be rubbed into a smooth paste with a stout rod. If the cake does not soften readily, it is covered with water and the crucible left for some time on the water bath or steam box. When finally soft and free from lumps, the material is washed into a porcelain dish or casserole. If the analysis is to be pushed along rapidly time can be saved by transferring the sintered mass directly to the casserole with a little water and boiling it gently for a few minutes. Persistent lumps can be crushed with an agate pestle. In any event, one way or the other,

the mass is to be softened and boiled a few minutes with water. It is then filtered and washed with hot water till filtrate and washings amount to about 250 cubic centimeters (Note 5). This liquid containing the alkaline chlorides and excess of lime is heated to boiling after the addition of 2 to 3 cc. ammonium hydroxide. It is then removed from the heat and ammonium carbonate solution containing 1.5 to 2 g. added in a slow stream (Note 6) after which the heating is continued short of boiling for three or four minutes, and the solution then set aside for the precipitated calcium carbonate to settle. While still hot it is filtered, the filtrate being received in a large porcelain dish. The transfer of the precipitate to the filter, rinsing out of the beaker and washing of the precipitate is done with hot water. Carbonate adhering to the beaker need not be rubbed loose (Note 7). The precipitate on the paper is washed free from chlorides. Filtrate and washings in the large dish are then heated short of boiling or are left on the steam box over night till the liquid is evaporated to about 25 cc. (Note 8). If on standing on the steam box it has gone to dryness, this amount of water is added and thoroughly rubbed up with the residue. The small amount of liquid is then transferred to a smaller dish or casserole (Note 9) and the evaporation carried on to dryness after which the residue so obtained is ignited carefully over a free flame till no more white fumes of ammonium chloride are given off (Note 10). During the ignition there will be considerable blackening due to organic matter in the ammonium carbonate. This as a rule burns white, but if thoroughly charred it will be sufficient since the carbon is insoluble and will be removed by the next filtration.

The residue consisting of sodium and potassium chlorides together with a little calcium salt that escaped the first precipitation is dissolved in 10 to 15 cc. hot water, one or two drops of barium chloride added to precipitate any sulphate present (Note 11) and, without filtering, about 0.5 g. of ammonium carbonate together with a crystal of ammonium oxalate to remove the excess of barium and the last portions of the calcium salts. After standing a few minutes the mixture is filtered through a 7 cm. filter into a small weighed porcelain dish, the filter and insoluble matter being washed about five times with hot water using only a small amount each time (Note 8). Three or four drops of hydrochloric acid are

then added to the filtrate and the dish placed on a water bath for evaporation. When dry the residue is ignited to expel ammonium salts (Note 10) and the dish cooled in a desiccator and weighed. The residue now consists of sodium and potassium chlorides and if not white after the ignition, it should be washed out of the dish with a little hot water into a small beaker from which it must be filtered again into the dish. The original small filter if still in place can be used. The solution is again evaporated and the residue ignited as before.

4. Precipitation and Weighing of Potassium Platonic Chloride. After the weight of the mixed chlorides has been obtained they are dissolved in the minimum quantity of hot water and transferred to a small beaker. A slight excess of platinum chloride solution (Note 12) is then added and the beaker set on the water bath for evaporation to dryness as complete precipitation of the potassium is not obtained without this. The dry residue must not remain on the bath after the liquid is evaporated since it might decompose. If the chemist cannot be at hand when all but the last drop of the liquid is gone the flame under the bath should be turned low towards the end so the water does not boil, though even under these conditions long standing is to be avoided.

The residue consisting of  $\text{Na}_2\text{PtCl}_6$ ,  $\text{K}_2\text{PtCl}_6$  and  $\text{H}_2\text{PtCl}_6$  is treated with about 15 cc. of alcohol 80% by volume (Note 13) which dissolves all but the potassium salt, and is filtered through a Gooch crucible (55). (See also Note 14.) The  $\text{K}_2\text{PtCl}_6$  is washed in the crucible with alcohol till the washings are no longer colored and then four or five times more, after which crucible and precipitate are dried at about 110 degrees and weighed.

The weights of KCl and  $\text{K}_2\text{O}$  are calculated from the weight of  $\text{K}_2\text{PtCl}_6$  found and from this and the weight of KCl and NaCl obtained above the  $\text{Na}_2\text{O}$  is calculated. The results are reported as percentages of  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$ .

**Notes.** 1. If lithium is present it will be weighed with the mixed chlorides but will not affect the precipitation of the potassium.

2. The platinum crucible used for the decomposition should have a capacity of at least 20 cc., but may be larger without harm. The ammonium chloride and calcium carbonate must be pure. It was formerly necessary for the chemist to prepare his own calcium carbonate but at present the salt especially prepared for this method

is on the market. It is rarely if ever entirely free from alkalis and consequently a blank must be run on each lot and a correction applied. In a commercial laboratory a quantity of the reagents is purchased, and a careful blank run. This will then serve till the stock is exhausted.

3. The object of covering the bottom of the crucible with carbonate is to prevent the sintered mass from sticking to it. The layer on top serves to prevent loss of alkaline chlorides by volatilization. For the same reason the crucible must be provided with a well fitting lid. Occasionally silicates very high in iron are met with which form fusible compounds under the conditions of the J. L. Smith method as ordinarily carried out. To prevent this, relatively more calcium carbonate than called for in the procedure above must be used.

4. The completeness of decomposition can easily be tested by treating the residue, after extraction of the sintered mass with water, with dilute hydrochloric acid. It should dissolve completely.

5. Complete extraction of the alkaline chlorides from the sintered mass, after boiling it with water, cannot be determined by testing the washings with silver nitrate as would at first suggest itself, for the reason that an oxychloride of calcium is formed which dissolves so slowly that the chlorine test would be given long after the more readily soluble chlorides of sodium and potassium had been removed. Experience has proven that a total filtrate and washings of 250 cc. is sufficient.

6. The solution of the ammonium carbonate should be started some time before it will be needed as it dissolves rather slowly and cannot be hastened by heating since this would occasion decomposition. The solution can, however, be made almost instantaneous by first grinding the salt fine in a mortar.

7. The precipitate of calcium carbonate is washed with hot water although an appreciable amount is soluble. This could be prevented by putting a little ammonium carbonate into the water but since provision must in any event be made for removing the further small amount that will be obtained on concentrating the large volume of liquid, it is not worth while. Both can be removed together.

8. Especial attention must be given to the fact that several times in the course of the operations of this method the whole

amount of the substance is in a very small volume of liquid and that this small volume of liquid must frequently be transferred from one vessel to another, sometimes with intermediate filtration. The loss of one drop might therefore at times cause a considerable error.

9. The details of manipulation involved in evaporating to dryness the filtrate from the calcium carbonate and igniting the residue (Note 10) may of course be varied according to circumstances. If the evaporating is done while the chemist is in the laboratory, a four-inch or even three-inch casserole may be filled and as this first portion evaporates, more can be added from time to time till the whole liquid has been transferred. The ignition of the ammonium salts can be done directly in the casserole without transferring to a small dish. With some little management also, the residue in the large dish referred to above can be ignited without transferring it. Such details of manipulation must however be thought out carefully before they are put into practice.

10. Considerable skill is necessary to drive off the ammonium salts without mechanical loss due to decrepitation. If, after the residue has become dry on the water bath or steam box, it be heated for a while at a temperature considerably above 100° but yet short of the point of decrepitation, the enclosed water is driven off quietly and the subsequent volatilization of the ammonium salts can be carried out with relatively little trouble. A good plan also is to heat the dish for a while on the sand bath. Another scheme would be to set one of the cylindrical, iron flame protectors on the hot plate on the desk and place the dish or casserole on the top. Still other arrangements with the apparatus at hand can be devised with a little ingenuity. Regarding the temperature of ignition, the rule is to heat short of the point of fusion of the chlorides of sodium and potassium, since above this there is danger of volatilization.

11. In the case of rock material very little sulphate is likely to be present. Still, it is necessary to remove it for two reasons. It would be weighed with the mixed alkalis as alkaline sulphate and would also contaminate the precipitate of potassium platinic chloride with sodium sulphate. The excess of barium must of course be removed as well as the trace of calcium still remaining. The purpose of the ammonium oxalate is to remove the latter which it does better than ammonium carbonate.

12. The platinum compound usually called platinic chloride is not a chloride but an acid with the formula  $H_2PtCl_6 \cdot 6H_2O$ . In the reaction, potassium takes the place of the hydrogen to form  $K_2PtCl_6$ . Most text-books call for a solution of such strength that 1 cc. = 0.1 g. Pt. The advantage of as strong a solution as this lies in the fact that a relatively small volume of liquid is used and therefore the time of evaporation is somewhat reduced. It is, however, such an expensive reagent — 1 cc. of this strength being worth about 10 cents — that it is better perhaps for beginners to use it in a more dilute solution. In precipitating the potassium it is deemed necessary to add sufficient platinum to react also with the sodium present to form sodium platinic chloride  $Na_2PtCl_6$ , which is soluble in alcohol. This gives a simple rule for calculating the amount of platinum to use: Assume the weight of mixed chlorides obtained to consist of NaCl alone and calculate how much platinum will be required to react with it. The relation between the NaCl,  $H_2PtCl_6$  and the strength of the Pt solution should be combined into one factor called A. Then the formula would be, Weight of mixed chlorides times A = cubic centimeters of platinum solution to use.

13. Alcohol 80% by volume has a specific gravity of 0.8645. It must be tested with a hydrometer.

14. In addition to the filtration and drying of the potassium platinic chloride in a Gooch crucible, two other plans are available: (a) The use of tared filters as described in section 63, and (b) Dissolving the precipitate and weighing the residue after evaporation to dryness. After filtration and washing in a filter, a weighed dish is placed under the funnel and the precipitate dissolved through with hot water. This solution is evaporated to dryness on the water bath and the residue dried at about 100° and weighed.

15. Since the account of this method is written primarily for beginning students in large classes no mention has been made of the use of platinum vessels excepting where absolutely necessary. Very accurate work would demand the use of platinum dishes for the evaporation of the filtrate from the carbonate precipitate and for the final ignition and weighing of the two chlorides. Porcelain, however, if controlled by a blank will serve very well.

## XII. THE DETERMINATION OF NITROGEN BY THE KJELDAHL METHOD.

The determination of nitrogen is frequently called for, especially in agricultural and food analysis, and this method devised by Kjeldahl is the one almost universally employed at the present time. Briefly the method consists in boiling the sample in concentrated sulphuric acid which oxidizes the carbonaceous matter and converts the nitrogen into ammonia. This at once reacts with the excess of acid forming ammonium sulphate. The acid solution is then diluted, an excess of caustic soda added and the mixture distilled. The ammonia set free is received in a measured volume of standard acid, the excess of which is titrated with alkali. See also the modification for nitrates below.

This method for the determination of nitrogen is not only of great practical importance, but it also illustrates in an admirable way many new points in manipulation and planning of the details of a long process. Commercial fertilizers will be employed as samples in the practice work and the discussion below is based on their characteristics and content of nitrogen. Consisting as they do of all sorts of mineral and organic matter both animal and vegetable, and varying from a few tenths of one per cent. of nitrogen to ten or twelve per cent., it is seen that a scheme that will serve under all these conditions is of well nigh general application.

According to the plan as outlined above, the unknown amount of  $\text{NH}_3$  evolved by the distillation of the sample is received in a measured portion of standard acid which must be more than enough to neutralize it. If the relation of this measured portion of acid to a standard alkali be known, for example, a pipetteful of acid = 30 cc. standard alkali, then, by titrating the acid not neutralized by the  $\text{NH}_3$  from the sample, the difference between the result so obtained and 30 cc. will give the value of the  $\text{NH}_3$  in the sample. This is made clearer by supposing the standard alkali to be a solution of  $\text{NH}_3$ , for instance 0.2N  $\text{NH}_3$ . Suppose 1 gram of sample to have been taken, and the following results obtained:

Pipetteful acid = .....	30.0 cc.	0.2N NH <sub>3</sub>
After distillation = .....	20.5 cc.	"
NH <sub>3</sub> in sample equivalent to = .....	9.5 cc.	"

1 cc. of 0.2N NH<sub>3</sub> = 0.00341 g. NH<sub>3</sub>.  $0.00341 \times 9.5 = 0.0324$   
g. = NH<sub>3</sub> in sample = 3.24%. Note: nitrogen in fertilizers is reported as NH<sub>3</sub>.

Had 1.023 g. = three times the factor weight for 0.2N alkali been taken as sample, 9.5 divided by 3 would have given the percentage directly.

It is especially to be noted that neither the exact strength nor the exact volume of the acid which receives the distillate need be known. All that is necessary in its measurement is that exactly the same volume be used each time. (See below for proper concentration of this acid.)

**Standard Acid for Receiving the Distillate.** The strength, and the volume to be used depends on the amount of ammonia in that portion of the sample that is subjected to distillation. In the case of fertilizers it is rare that one containing more than 6 to 7% will be encountered; therefore with one gram of sample, provision for 0.1 g. NH<sub>3</sub>, equivalent to 10%, will be ample. When certain material such as dried blood, Chile saltpeter, etc., running from 11 to 15% are analyzed, a double portion of acid can be used. The concentration of the acid then, should be such that the pipetteful employed will absorb 0.1 g. NH<sub>3</sub>. The solution may be either hydrochloric or sulphuric acid, though in this exercise sulphuric will be required in order to give more practice in making standard solutions.

The pipette for its handling (see below under Apparatus) is first selected and then, from the specific gravity and percentage purity of the strong acid, about a liter of solution should be made of such strength that a pipetteful will absorb approximately 0.1 g. NH<sub>3</sub>. The exact volume relation of a pipetteful to the standard alkaline solution below is found by titration.

**Standard Alkali.** A solution of ammonium hydroxide is usually employed, presumably because the neutralization is begun with the NH<sub>3</sub> from the sample and there is some point in finishing with the same substance. As a matter of fact, though, caustic soda

or potash would serve as well. The strength of the solution is determined here as in all cases by the amount of substance to be titrated, the accuracy required and the nature of the solution itself. Ammonia being volatile, it is obvious that a very strong solution is not stable. The odor of  $\text{NH}_3$  is apparent over a 0.5N solution. Still, if a solution of this strength were kept in a bottle permanently connected with a burette into which it could be allowed to siphon as needed, it would be stable enough for use, because under these conditions the atmosphere of the bottle above the solution would soon become saturated with  $\text{NH}_3$  which would then prevent further loss. If, however, the solution must be poured from the bottle into a burette the loss of  $\text{NH}_3$  is considerable.

At a dilution of 0.2N or less, ammonia solutions are fairly stable and will bear pouring. The best procedure for the student in this practice work, is to make the solution approximately 0.2N by diluting the proper volume of strong ammonium hydroxide and then determine its exact strength by titration against the standard acid prepared in Practice IV., using cochineal (111, 4) as indicator. The normality (107, 6) is then calculated and the factor weight of sample (107, 7) to be used with it. Usually two or three times the factor weight is used in an analysis.

**Apparatus.** (1) Pipette. For measuring the standard acid, a 10 or 25 cc. pipette will be wanted. This need not be calibrated but its outflow should be regulated (86, 1) and in its use all the precautions necessary to insure constant delivery must be observed (86, 2).

(2) Kjeldahl Digestion Flasks. These are round bottom flasks made of Jena or other hard glass to withstand boiling sulphuric acid. Two sizes are in common use: one, about 200 cc. in capacity, is employed when the solution or some aliquot part of it is to be transferred to another flask for distillation, and the other, about 600 cc., is used when the whole solution is to be distilled. (See below under Amount of Sample.)

(3) Condenser. Fig. 6,D. The best condenser for this distillation is one in which the inner tube is of block tin. For beginners, however, an ordinary glass one will serve every purpose. Before using it for a determination it should be steamed out. This is done by setting up the apparatus as for distillation and boiling water in the flask but without allowing the condensing water

to flow through the outside jacket. Treatment with steam in this way dissolves the alkali from the surface of the glass and renders it less likely to attack when used subsequently in an analysis. The small amount of alkali still given up to the distillates will be regular and may be corrected in the blank.

(4) Distillation Flask. Fig. 6,A. This should have a capacity

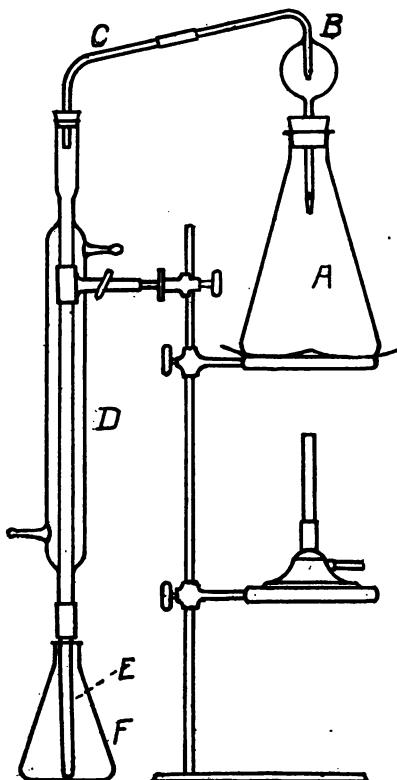


FIG. 6.

of from 600 to 700 cc. The form has no significance as it may be round bottom, flat bottom or of the Erlenmeyer type.

(5) Distillation Tube. Fig. 6,B. This is for connecting the flask to the condenser and consists of a properly bent tube with a bulb blown near the middle. Such tubes are made in a variety of shapes and are usually provided with traps to prevent carrying over of caustic soda in spray.

(6) Receiving Flask for Distillate. Fig. 6,F. Since the titration can be made directly in this flask it is most convenient if of the Erlenmeyer pattern with a capacity of 300 to 400 cc. A glass tube for conveying the distillate into this flask must also be provided (Fig. 6,E). It is attached to the lower end of the condenser with a piece of rubber tubing and should reach to the bottom so its lower end will be below the surface of the standard acid.

(7) Assembling the Distillation Apparatus. Figure 6 indicates a method of assembling the various parts for the distillation. The plan is of course capable of many modifications, but for use in the rather confined working space allotted to a student, the above compact scheme is believed to be the best. Rubber stoppers and rubber tubing may be used for making the various connections. As a rule, the tube B is bent at such an angle as to require the insertion of an extra piece C in order to make the connection with the condenser in a vertical position. (See page 181 for general observations on apparatus building.)

**Special Reagents.** (1) Concentrated Sulphuric Acid. This is used for the digestion or solution of the sample. It should be the strong, 1.84 sp. gr., acid.

(2) Caustic Soda Solution. No particular strength is necessary, anything from 20 to 40% being sufficient. It may be made from commercial NaOH. The strength with reference to the sulphuric acid above is roughly determined as follows: 5 cc. of the concentrated acid are diluted in a beaker to about 200 cc. Any convenient indicator is then added and neutralization brought about by pouring in the caustic soda solution from a cylindrical graduate. On the basis of the results obtained the quantity of soda solution to be used in a distillation can be estimated. A good rule is to add enough to neutralize all of the acid employed in dissolving the sample, assuming none to be lost thereby, and about 5 cc. in excess. When, however, the acid solution of the sample is diluted and only an aliquot part used for the distillation, calculation is made on the basis of the same aliquot part of the original acid. (See Procedure below.)

(3) Potassium Sulphate. This should be free from nitrogen. It must be at least coarsely pulverized if not in small crystals when obtained.

(4) In addition to the above, each student should supply himself with about 10 g. of granulated zinc and a piece of paraffine the size of a small walnut.

The procedure below should be read through and the amounts of the various reagents for one determination noted. Five or six times these quantities should then be provided. (See Note 4 for blank on reagents.)

**Amount of Sample.** One of two general procedures can be followed: (1) A portion of about a gram, or three times the factor weight for the standard alkali, may be digested, the solution diluted, treated with soda, etc., and distilled. (2) A larger portion, for example ten times the factor weight, may be digested, the solution diluted in a graduated flask and an aliquot part taken for the distillation. In the first case it is obviously advantageous to use the 600 cc. size digestion flask as then the dilution, treatment with soda, etc., can be made in it after which it can be connected to the condenser and the distillation made without the necessity of transferring the liquid. On the other hand, fertilizers are usually rough samples, consisting of a mixture of materials of widely different specific gravity, thus making it difficult to weigh a small portion that will be representative. Beginners will therefore do well to follow the second procedure. Either size digestion flask may be used.

Ten times the factor weight—3.41 g. in the case of 0.2N alkali—should be weighed and the solution diluted in a 250 or 500 cc. flask. Enough should then be taken for the distillation to give at least twice the factor weight (Note 1).

Owing to the rough character of the material, extra care must be used to insure a thorough mixing of the contents of the bottle before taking the small portion to be weighed.

**Procedure.** The weighed sample (see above) is transferred to the bottom of the digestion flask by the method described in the second paragraph of section 37, 1. Approximately 10 g. (72) of potassium sulphate are then added and 20 to 25 cc. of concentrated sulphuric acid. (25 cc. are used for the larger amount of sample.) The acid is mixed with the sample by giving the flask a gentle rotary motion and warming the bottom over a low flame. Care must be taken not to get the mixture far up on the sides of the flask as it is sometimes difficult to wash it down in the

subsequent digestion. When sample and acid are mixed the flask is set at an angle of about 45 degrees on a hole cut in a square of asbestos board. The diameter of this hole should permit heating as much of the bottom of the flask as possible and yet prevent the flame from reaching above the level of the acid. The heating is started with the flame just short of touching the flask, but after ten minutes or so when frothing has ceased it may be turned up and allowed to play against the bottom. The mixture at first blackens but after some time begins to show a lighter color till, in the course of an hour or so, it is colorless or at least pale yellow. This marks the end of the digestion, though prolonging it somewhat does no harm. An occasional sample is encountered that froths very badly, in which case a piece of paraffine the size of a pea may be added (Note 3). When the digestion is completed, the flask is allowed to cool and the contents diluted by adding rapidly in a full stream 75 to 100 cc. of water. If the liquid in the flask stands too long before dilution, a solid cake may form, in which case no particular caution need be observed in adding the water, as the cake dissolves slowly.

After the dilution in the digestion flask the procedure varies depending upon the general plan of the work. If only about a gram of sample has been dissolved (see above) and the whole amount is to be distilled, the liquid is transferred at once to the distillation flask unless a large size digestion flask has been used in which case after addition of soda, etc., as described below it is connected to the condenser and distilled.

If three or four grams of sample have been dissolved, the contents of the digestion flask are transferred (65) to a graduated flask, diluted to the mark and mixed. Insoluble material, if any remains after the treatment with acid, need not be washed out as it contains no nitrogen. It is also not necessary to filter the solution or wait for it to settle, but the appropriate aliquot part (see above) may be at once pipetted into the distillation flask.

Preparation for the distillation is begun by first rinsing the different pieces of the apparatus to remove any ammonium chloride that may have deposited, and then connecting them as in Fig. 6. A pipetteful of standard sulphuric acid is put into the receiving flask together with the indicator for the subsequent titration. A possible high-ammonia sample will then show itself by giving an

alkaline color to the distillate, upon which another pipetteful of standard acid can be added. Appropriate corrections are made in the titration and the determination is thus saved.

When the apparatus is ready, attention is turned to the solution in the distillation flask. About 5 cc. more caustic soda solution than is needed for the neutralization of the acid (see above) is added by pouring it down the side of the flask which should be inclined for the purpose. It is done in this way so it will sink at once to the bottom leaving an acid layer on top thus effectually preventing the escape of ammonia before connection is made with the condenser. After the soda, 3 to 4 g. granulated zinc, previously rinsed in a beaker with a little water, are added and also a piece of paraffine the size of a pea. The zinc by causing a slow evolution of hydrogen prevents bumping and the paraffine prevents foaming during distillation.

When connection has been made with the condenser, the contents of the flask are mixed by gently shaking. The heating is best done on a wire gauze. It is started cautiously at first and finally raised so the mixture in the flask boils as rapidly as may be and not cause frothing or boiling over. When about 150 cc. have distilled it is assumed that all ammonia is over. The flame is then turned out and the stopper at once removed from the flask to prevent a sudden sucking back of the distillate.

The receiving flask is now disconnected, the tube E is rinsed off and laid aside and the excess of acid titrated with the standard ammonia. The results are calculated as percentage of NH<sub>3</sub>.

**Notes.** 1. When a large amount of sample is dissolved, diluted to a definite volume and an aliquot part of the solution taken, this aliquot part may represent a smaller quantity of the original sample than would be permissible if it were weighed directly.

2. The addition of the potassium sulphate raises the boiling point of the acid and thereby hastens the digestion. This plan is known as the Gunning modification. In the earlier method an increased rate of oxidation was obtained by the catalytic action of mercury salts. About 0.6 g. of metallic mercury or an equivalent amount of mercuric oxide was added. The mercuric sulphate formed accelerated the oxidizing action of the acid. Since mercury forms compounds with ammonia which are not easily broken up

by alkali it was necessary in this method, after dilution, to add sufficient potassium sulphide to react with the mercury. The resulting sulphide of mercury was not filtered, as when once precipitated it remained insoluble and no longer affected the ammonium salts.

3. It frequently happens that black particles persist on the sides of the digestion flask after the main portion of the solution has become colorless or nearly so. As a rule no attention need be paid to these as they gradually disappear on continuing the boiling. Their oxidation may be hastened, however, by carefully inclining the flask till the hot acid liquid touches them. Great care must be used in doing this on account of the high temperature of the solution.

4. The reagents employed are rarely free from nitrogen so a blank is necessary. A mere mixing of the reagents, however, and carrying them through the operation is not sufficient. The organic matter in the sample owing to its reducing action might decompose traces of nitrates that in a straight blank would escape. It is customary therefore to add a few tenths of a gram of pure sugar.

5. The Kjeldahl process being a long one it often becomes necessary to allow the solutions to stand for some time. If this is done it should be remembered that all acid solutions absorb ammonia and therefore, at certain stages at least, the flasks must be securely closed with rubber stoppers before being set aside.

#### **Modification for Nitrates.**

The method as outlined above obviously would not include nitrogen in the form of nitrates or nitrites. These compounds would be partially but not entirely reduced by the organic matter usually present. Most of the nitrogen would escape in the form of nitric acid due to the action of the less volatile sulphuric acid. It becomes necessary, then, to modify the reagents in such a way as to prevent this escape of nitric acid and convert it into ammonium compounds. This can not be done directly but if a substance like salicylic acid be dissolved in the sulphuric acid with which the sample is treated, the nitrate is changed to a nitro-phenol. These nitro-phenols when acted upon by strong reducing agents

are changed to amino-phenols, compounds in which the nitrogen is in the  $\text{NH}_2$  group. This, by the action of the hot acid, is converted into ammonium sulphate. Sodium thiosulphate is used as the reducing agent. The same considerations governing the amount of sample, etc., hold for this modification as for the other method.

**Special reagents.** In addition to those of the regular method above, there will be required some concentrated sulphuric acid, sp. gr. 1.84, in which salicylic acid is dissolved at the rate of 3.3 g. per 100 cc.; and also some solid sodium thiosulphate. A blank should be run on these reagents.

**Procedure for Nitrates.** The sample is weighed into the digestion flask as described above, and 30 to 35 cc. of the salicylic-sulphuric acid reagent added and mixed thoroughly with the sample, (Note 1) the mixture being allowed to stand five or ten minutes with occasional gentle shaking. Approximately 5 g. of sodium thiosulphate and 10 g. of potassium sulphate are then added and the heating begun, cautiously at first and finally with rapid boiling till the solution is colorless or nearly so. The dilution and distillation are carried out exactly as described above.

**Notes.** (1) An important point in the handling of this method is to secure intimate contact between all portions of the nitrate and the salicylic-sulphuric acid mixture. In the case of pure Chile saltpeter or samples containing a large admixture of this material it is advisable, after introducing the weighed portion into the flask, to add a few cubic centimeters of water to dissolve the nitrate. This is then evaporated so that a thin layer is deposited over the bottom of the flask. Under these conditions the acid mixture is surer in its action. Another plan is to grind the sample with an equal weight of some inert material such as gypsum. When working with material known to be high in nitrate it is best not to use more than a gram for the digestion.

(2) The test for nitrates is made as follows: About two grams of the fertilizer are shaken up with 15 to 20 cc. of water. This is then filtered or allowed to settle and a portion of the clear liquid treated in a test tube with an equal volume of concentrated sulphuric acid with which it is thoroughly mixed. The tube is then cooled and a little ferrous sulphate solution poured down the side in such a way as to cause it to float on the acid mixture. The appearance of a brown or black ring at the juncture of the two

liquids shows the presence of nitrates. The ferrous solution should be rather strong and clear green in color. At least five minutes must be given for the appearance of the "ring."

### XIII. DETERMINATION OF CARBON DIOXIDE.

Some form of decomposition of the sample that will set the carbon dioxide free, is the starting point of all methods for its determination. This can be accomplished by ignition, by fusion with acid fluxes and by treatment with acids. The measurement of the gas after it is set free can be done in a variety of ways: (1) Its volume can be determined. (2) It can be absorbed in a suitable reagent and the increase in weight noted. (3) The loss in weight of the sample due to the expulsion of the carbon dioxide can be found. Each plan requires its special form of apparatus and has its special limitations. The second, however, may be considered the most important and is the one selected for this practice work. The method in brief consists in treating the sample in a flask with hot, dilute acid and passing the evolved carbon dioxide into caustic potash solution or soda lime contained in a vessel suitable for weighing. This simple statement, however, gives no idea of the manipulative difficulties involved. On referring to the previous methods in which a gas was handled quantitatively, that of pyrolusite, page 181, and of nitrogen, page 208, it will be seen that the apparatus required was relatively simple because no attention was given to the gases and vapors accompanying those that were to be determined. In contrast with this, the method of measurement of carbon dioxide requires its sharp separation from the mixture of air, water vapor, acid fumes and other gases that may be generated in the solution of the sample. There is demanded, therefore, a more complicated apparatus in the various parts of which special reagents are placed to remove the substances that would otherwise be absorbed along with the carbon dioxide. The method has indeed been selected with special reference to giving practice in the construction and use of such an apparatus and the student should accordingly give as much study to this point as to the determination itself.

**Details of the Apparatus.** (See figure 7 and Note 1.) A is the decomposition flask. It should have a capacity of 100 to 250 cc. and may be of any design. It is fitted with a two-hole stopper carrying the small separatory funnel C for introducing the acid

and the glass tube E for conveying the evolved gases to the first reagent bottle G.

The tube E is provided with the jacket F through which cold water is circulated to condense the bulk of the steam from the boiling liquid in A. This jacket consists of a tube about 8 inches long and one inch in diameter and connects with E by means of two-hole stoppers. Care must be exercised in bending E so that the lengths of the several parts correspond to the design in figure 7. Particular attention must be given to the bend just above the flask. This is necessary to provide space for the bulb of the funnel but it must be made flat enough to permit the passage of the jacket tube.

The wide mouth bottle G has a capacity of about 60 cc. and is half filled with concentrated sulphuric acid, the purpose of which is to remove the water that escapes condensation in E. This bottle is connected by the tube H with a similar bottle I containing a saturated solution of silver sulphate (see below) in dilute sulphuric acid (equal parts acid and water). The function of the silver sulphate is to precipitate any hydrochloric acid and hydrogen sulphide that may be carried over, while the sulphuric acid lowers the vapor pressure of the solution and thus protects the calcium chloride in the next tube (Note 1).

After passing through I the stream of gas is conducted by means of J into the 6-inch U-tube K containing granular calcium chloride (see below; also Note 2) by which the water vapor taken up in I is removed. The mixed gases now consist only of carbon dioxide and the nitrogen and oxygen of the air. From K they pass into the first part of the absorption train as it is called, that is, that part of the apparatus in which the CO<sub>2</sub> is absorbed and weighed. In figure 7 a Liebig potash bulb L is indicated, this being the simplest and cheapest form. It is connected directly to K and contains a solution of caustic potash (see below) which absorbs all but possible traces of the carbon dioxide and permits the passage of the oxygen and nitrogen of the air. Immediately connected with L is the small 3-inch U-tube M the first limb of which is filled with granular soda lime (see below) and the second with calcium chloride. The soda lime next to L serves to retain any CO<sub>2</sub> that escapes absorption in the potash solution and the calcium chloride takes up the water vapor carried out of L by the unabsorbed air. (See also Note 3.)

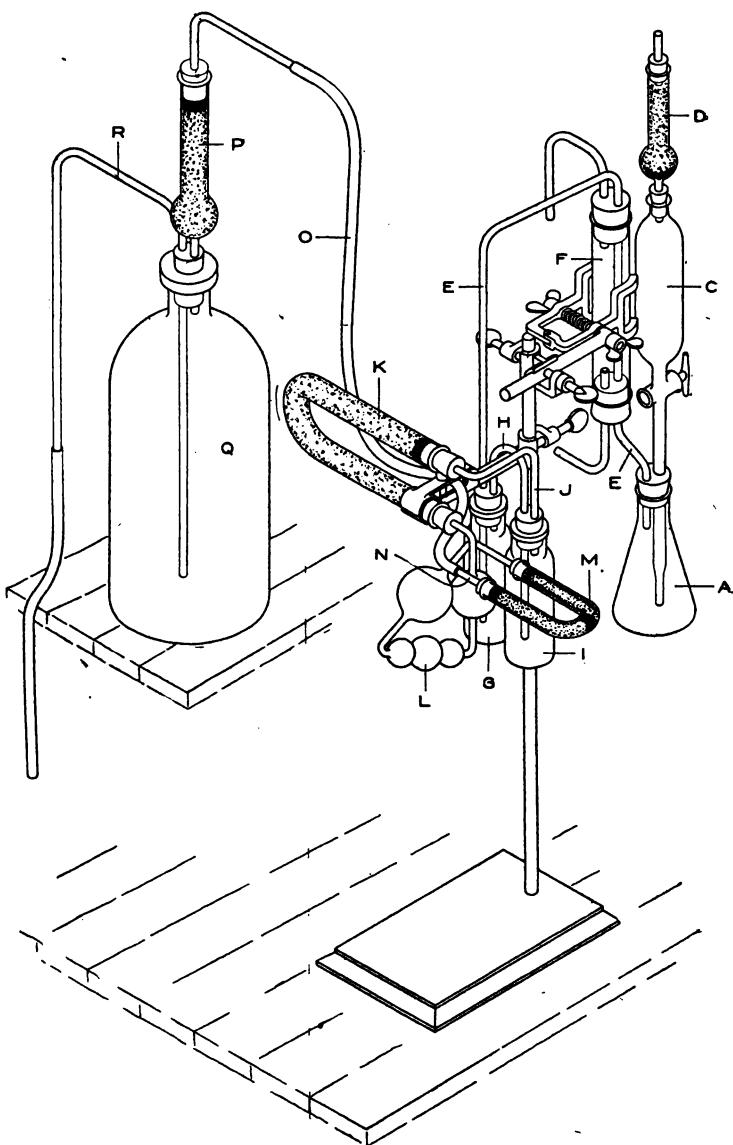


FIG. 7.

Since L and M are to be weighed, means must be provided for closing them when disconnected from the apparatus. This is usually done by caps made from short pieces of soft gum tubing closed at one end with small glass plugs. These are slipped over the open end of the potash bulb when it is drawn out of the stopper in K and over the short tube N in the stopper of M. A glass plug should also be provided for closing the U-tube K when the potash bulb is removed.

For drawing air through the apparatus an aspirator Q must be provided. This can be a tubulated bottle or an ordinary five-pint acid bottle fitted with a two-hole stopper carrying a siphon tube R as shown in figure 7. This is in every way as satisfactory as the more expensive tubulated aspirator bottles, provided attention is given to the length of R. This must be several feet so there will be sufficient head to insure a steady flow. The bottle Q should be set on a support on the desk so R can drain directly into the sink. It is well also to provide a screw pinch-cock for its lower end to regulate the rate of flow. The aspirator is connected to N by means of soft gum tubing O. P is a tube filled in its lower half with calcium chloride and the upper half with soda-lime. It serves as a guard tube to prevent any water vapor or carbon dioxide from entering M.

A guard tube D filled with soda-lime is also provided for the funnel C, so that when air is drawn through the apparatus it will be free from CO<sub>2</sub>.

**Special Reagents.** 1. Silver Sulphate Solution. About a gram of silver nitrate is dissolved in a casserole in a little water and 3 to 4 cc. concentrated sulphuric acid added. A cover glass is then put on and the mixture boiled down till copious white fumes are given off. After cooling, the residue is diluted to about 150 cc. It need not be filtered.

2. Soda-Lime. Large lumps should be crushed and only pieces about the size of a small pea used. These can easily be separated by means of two sieves of proper mesh.

3. Calcium Chloride. The granular, not the fused variety should be used, pieces about the size of small peas being employed as for soda-lime above. Calcium chloride usually contains small amounts of calcium oxide which would absorb carbon dioxide, and it is therefore necessary to saturate it with the

gas before using it in a determination. This can be done by keeping the stock of chloride in an atmosphere of dry carbon dioxide or by generating the gas in the evolution flask of the apparatus. The latter plan is perhaps the better for students and is carried out as follows: The apparatus is set up with the bottles G and I and the U-tube K connected and filled but omitting the absorption train. Carbon dioxide is then generated in the flask by means of marble and hydrochloric acid and allowed to flow through the bottles and U-tubes for 20 to 30 minutes. It is a good plan, if the work can be so arranged, to leave an atmosphere of  $\text{CO}_2$  in the apparatus over night. Finally, after the chloride has been saturated with the gas, the flask is cleaned and again connected. The guard tube D is put into place, the aspirator connected with K and 5 to 6 liters of air drawn through to remove the excess of carbon dioxide.

4. Potassium Hydroxide Solution. About 250 cc. should be prepared by dissolving the solid in approximately twice its weight of water. It often contains substances that take up oxygen from the air thereby causing an increase in weight. These can be destroyed by heating the solution nearly to boiling and dropping into it with constant stirring a dilute solution of potassium permanganate until a slight permanent green color is produced. The mixture is then cooled and preserved in a tightly stoppered bottle. The green color will soon fade and a brown precipitate settle out but this in no wise affects the reagent as an absorbent for carbon dioxide.

**Testing the Train.** After the various bottles and tubes have been filled with their appropriate reagents and put together to form the complete apparatus, two tests must be made.

(a) The aspirator bottle, filled to give the maximum pressure, is connected and the stopcock of the funnel closed. Bubbling through the solutions should cease in a minute or so which shows that the various connections are air-tight. A few bubbles per minute are, however, allowable.

(b) When the train is shown to be air-tight, the potash bulb and U-tubes are disconnected (Note 6), and, after closing the ends with the plugs and caps, they are weighed (Note 7) and again attached to the train and 1500 cc. of air aspirated through, at the rate of about 75 cc. per minute (Note 8). Bulb

and U-tube are then weighed again. This "running to constant weight" should be continued till successive weighings agree within at least 0.0005 g.

It is well also to make a further test of the working of the apparatus by determining the carbon dioxide in a specimen of pure salt. For this purpose clear crystals of the mineral calcite ( $\text{CaCO}_3$ ) are frequently recommended. A more exact method is to use pure sodium carbonate prepared as described on page 160. Several grams can be ignited to constant weight, dissolved and diluted to a definite volume so that a pipetteful will contain at least 0.5 g. Successive portions of the solution can then be used.

**Procedure.** About a gram of sample is carefully weighed and transferred to the bottom of the flask A. The potash bulb and guard tube are weighed and connected. Thirty to forty cubic centimeters of water are added to the sample in the flask which is then connected with the apparatus. The separatory funnel is charged with 15 to 20 cc. dilute hydrochloric acid (1:1) and the guard tube D inserted. The aspirator is not attached till later. The cock is then opened and the acid allowed to drop (Note 9) slowly onto the sample, the rate being so regulated that the bubbles of gas do not pass through the liquid reagents faster than can conveniently be counted (Note 10). When all of the acid has been added the cock is closed and as the evolution of gas becomes slower the flask is gently warmed till the sample is all dissolved, care being taken not to allow the bubbling through the reagents to become too rapid. The solution in the flask is finally boiled for a few minutes after which the flame is removed and the funnel cock opened at once to prevent a "sucking back" of the liquid reagents in the apparatus. The heating of the flask and subsequent boiling is best managed with a small flame, holding the burner in the hand.

When the boiling is completed, the aspirator is connected and at least 3 liters of air drawn through, the first 500 cc. being at the rate of 40 to 50 cc. per minute (Note 8) and the remainder somewhat faster, 75 to 80 cc. per minute. The potash bulb and guard tube are then disconnected and weighed (Note 7) the increase in weight being the quantity of carbon dioxide in the sample.

**Notes.** 1. In constructing the carbon dioxide apparatus the student should aim to produce a craftsman-like piece of work, and to do this, careful attention must be given to the details of design and construction. The lengths of the various parts of the bent pieces and the character and angle of the bends must be studied. The sections on glass working should be reviewed. In making the Tube E the bend just above the flask must be made flat enough to permit the passage of the jacket tube. Especial attention is called to that feature of the design whereby all connections are accomplished without the use of rubber tubing. (The one leading to the aspirator is beyond the parts of the apparatus that are to be weighed and therefore does not need to be absolutely tight.) It might be said at this point that in apparatus building where it is necessary to connect two pieces of glass tubing, the plan of putting the ends together in a rubber stopper is far superior to the use of short pieces of rubber tubing. Another special feature of this design is that the assembling of the various parts requires nothing outside the ordinary stock of the chemical store room.

The complete apparatus should be built before any of the reagents are put into the bottles or tubes.

2. In drying a mixture of gases in an apparatus like the carbon train in which one of them is absorbed and weighed, it is necessary that the unabsorbed gases enter and leave the apparatus with the same content of moisture. In some forms the sulphuric acid wash bottle follows the silver sulphate solution in which case the gases enter the apparatus with less moisture than on leaving it because sulphuric acid is a more efficient drying agent than calcium chloride. To remedy this it is customary to moisten the plug of cotton in the first limb of the U-tube K with a few drops of water. By reversing the sulphuric acid and silver sulphate bottles, however, this is not necessary. The sulphuric acid in the silver solution is sufficiently dilute to allow the passage of some water vapor but there will not be enough to render the calcium chloride wet. The bottle containing the strong sulphuric acid serves as a guard or control by removing all the water and thus preventing the dilution of the silver sulphate solution.

Various other forms of drying apparatus and different reagents for removing hydrochloric acid and hydrogen sulphide are often used. Ambitious students are recommended to look up these and other points in the larger text-books.

3. In filling the various tubes with calcium chloride or soda-lime, the material is shaken down by tapping and is then held in place by inserting plugs of cotton or glass wool. When filling a straight tube a plug of cotton is first put into the lower end to support the material.

4. The Liebig potash bulb and small guard tube M are weighed together and must therefore be provided with a wire by which they can be suspended from the hook above the balance pan. Small brass wire serves the purpose. When connected with the apparatus it should hang in such a position that the row of small bulbs on the bottom are inclined upward at an angle of about thirty degrees.

Many other forms of potash bulbs are in use, one of the most common being the Geissler. This is so designed that it stands alone and has the soda-lime-calcium-chloride guard tube attached, the best form being that with a ground glass joint. It must be said, however, that such joints have the weakness of working loose and must therefore be held in place by means of a turn or two of small brass wire. While the drawing in figure 7 shows the Liebig design, students should have no difficulty in modifying it so as to use the Geissler or other forms of potash bulb.

Soda-lime alone can also be used for the absorption of CO<sub>2</sub>. In this case two 5-inch U-tubes can be employed. The first contains soda-lime and the second soda-lime in the first limb and calcium chloride in the second.

5. The potash bulbs are conveniently filled by sucking the solution into them from a small beaker. For this purpose it is best to attach a short piece of rubber tubing to use in the mouth. The right amount of solution is judged by drawing air through with the bulbs in the slanting position in which they hang on the apparatus. They should be as full as possible and yet be short of the point at which there is danger of drops of liquid being carried out by the stream of air. One filling can be trusted to absorb a gram of carbon dioxide.

6. Potash bulbs of whatever make are fragile pieces of apparatus and the student will therefore do well to practice connecting and disconnecting them before undertaking a quantitative experiment.

7. Owing to the large surface exposed, the weighing of the potash bulbs and guard tube requires careful attention (see 31). Students are advised to use the method of tares as described in 28. A good plan is to fill two sets of bulbs and guard tubes and use the heavier one for the first determinations. Some liquid can then be poured out to lighten it, after which it can be used as the tare and the other employed for absorbing CO<sub>2</sub>. Through apparently much more complicated, experience will show that the method of tares is really a time saving device in weighing bulky objects of this description. If the tare bulb is kept near the other one during the determination so it will be at the same temperature, the weighing may be made at once on the conclusion of the aspiration. Two clean pieces of cloth should be kept to throw over them during the determinations as a protection from dust.

8. The volume of air aspirated through the apparatus is readily measured by having the aspirator bottle marked with paper stickers at 500 cc. intervals, beginning at the top. Finer measurements are made by collecting the water from the aspirator in a graduated cylinder.

9. The stem of the separatory funnel should reach nearly to the bottom of the evolution flask so the lower end will be below the surface of the liquid. Another important point is to have the stem full of liquid. This is accomplished by contracting the tip somewhat and by frequent cleaning (2,3) so the glass is readily wet. The stem can also be filled with water before attaching the flask. This is then displaced by the acid, the stem remaining full till all the liquid is down.

10. In the case of a carbonate like dolomite which is insoluble in the cold, the acid is all allowed to flow into the flask after which the evolution of gas is started by heating.

#### XIV. THE ANALYSIS OF BRASS.

The important constituents of brass are zinc and copper, together with a small amount of lead. Tin, antimony and iron may also be present. Brasses as a rule are examined for tin, lead, copper and zinc, and accordingly the method outlined below assumes that only these metals are present. The scheme of analysis consists in dissolving the sample in nitric acid and evaporating to dryness to render any tin insoluble. This is filtered and the solution then evaporated with an excess of sulphuric acid to convert the lead into insoluble lead sulphate. Copper is electrolytically precipitated from the solution after which the zinc is separated as phosphate, ignited and weighed.

The essentially new point in procedure brought out in this exercise is the use of electrical energy as a precipitating agent. A thorough discussion of this method of precipitation and separation is matter for an entire chapter in analytical chemistry and therefore cannot be attempted here. Still, a student should not undertake even the simple electrolytic precipitation of copper as given below without some general notion of the principles involved.

A book on physics<sup>1</sup> should be reviewed and the definitions of ampere, volt, coulomb, electrode, cathode, anode, conductivity and resistance refreshed. The simple mathematical relations existing between the numerical values of amperage, voltage, conductivity and resistance should also be known. From a practical standpoint the different methods of connecting the several cells of a battery and the effect on the current should also be reviewed. Still more important is the use of the measuring instruments, the ammeter and voltmeter. A moment of careless ignorance may mean the destruction of an expensive piece of apparatus.

Every laboratory will have its peculiar electrical installation and no beginner should attempt its use till he can make a schematic drawing of the arrangement and carry through on paper the whole experiment. The following points bear especially upon electrolytic analysis.

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<sup>1</sup>Students will find no better opportunity than this for the cultivation of that best of habits: the use of knowledge gained in one department of the university to help in understanding what is studied in another.

**Important Points in Electrolytic Precipitation.**

(1) Electrolytic precipitations can be made only with a direct current. The alternating current is useless.

(2) The amount of substance precipitated in unit time is proportional to the current, that is, the amperage. Anything, therefore, that affects the current such as varying the temperature, the distance apart and size of the electrodes and the concentrations of the solution will change the rate of deposition.  $M = z I t$

(3) When a metal is precipitated and the current shut off, it immediately begins to dissolve, thereby producing a current in the opposite direction from the one that precipitated it. It is evident from this that the tendency to dissolve exists during the progress of the precipitation and that the pressure (voltage) of the precipitating current must be great enough to overcome this back pressure. This tendency to dissolve in a given medium is different for different metals and therefore the pressure of the precipitating current necessary to overcome it will vary according to the metal. From this it follows that if several metals are together in solution and they have widely different tendencies to dissolve they can be separated one after the other by starting with a voltage high enough to counteract the back pressure of one but not that of the others and when this one is all precipitated, the next in the series can be removed by increasing the voltage and so on. This is the principle on which electrolytic separations are made.

(4) The physical character of the precipitate is as important in electrolytic separations as in the case of those produced by purely chemical means. The deposit of metal should be pure and closely adherent. It may, however, be spongy, discolored and so loosely attached to the electrode as to make it impossible to handle. The causes of this are not well understood, though the following is generally true: (a) Some substances are more readily precipitated electrolytically in good physical condition than others. (b) The character of the solution from which the precipitation takes place affects the nature of the deposit, for example, the presence of substances that do not appear to enter into the chemical changes. (c) The form of combination in which the metal exists. It is frequently true that a better deposit is obtained from a complex compound like the metallo-cyanides. (d) Increase of tempera-

ture of the electrolytic bath affects the deposit by increasing the tendency towards sponginess. (e) Increasing the rate of current, or more properly, the current density, increases the danger of poor deposition. Current density is defined as the current per 100 square centimeters of electrode surface on which the deposition is taking place. It is usually written ND<sup>100</sup>. (f) The character of the surface of the electrode, whether it is polished or roughened with a sand blast, or whether it is a continuous sheet or woven gauze also has its influence. The roughened or gauze surface is necessary to retain certain deposits that have a strong natural tendency towards sponginess. Their use also counteracts other tendencies towards sponginess and permits a stronger current with those metals like copper that readily form good deposits, thereby cutting down the time required for the determination. (g) Stirring of the solution during the action of the current likewise seems to have a profound influence on the character of the deposit and in the sense that it improves it. The usual procedure is to rotate one of the electrodes, for example, the anode when a dish is used as cathode (Fig. 8). The effect is such that the current may be increased so that precipitations ordinarily requiring hours are completed in as many minutes. Finally, it is scarcely necessary to add, cleanliness of the surface promotes a good deposit.

(5) The shape or design of the electrode has very little to do with the deposit excepting in so far as the current density is affected. Platinum dishes and crucibles are perhaps most frequently used. They serve both as cathode and as container for the solution to be electrolyzed and have the advantage of retaining loosely adhering deposits better than the dipping electrodes. This type consists of a piece of platinum foil attached to a stout wire for connecting with the source of current. A large piece, usually from 80 to 100 square centimeters surface, counting both sides, is employed as cathode and a much smaller one as anode. (See figures 8 and 9.)

#### Determination of Tin.

**Procedure.** From 3 to 5 g. of drillings (36) are dissolved in a covered casserole in dilute nitric acid, heat being used if necessary towards the end. The cover glass is then rinsed off and the solution evaporated to dryness (64), finally on the water bath or

steam box. The residue is treated with enough nitric acid to moisten it thoroughly and then with sufficient water to dissolve everything but the white metastannic acid (Note 1). This is filtered, washed with hot water and ignited in a porcelain crucible according to 61, the ignition being carried to constant weight over the blast lamp. A Gooch crucible (55) may also be used for the ignition but on account of the blasting, it is better to employ a platinum one in this case.

The ignited compound is  $\text{SnO}_2$  from which the amount of tin is to be calculated.

#### Determination of Lead.

**Procedure.** The filtrate from the metastannic acid is evaporated almost or quite to dryness (Note 2) in a casserole and, after cooling, is treated with about 10 cc. of concentrated sulphuric acid. The cover glass is then put on and the liquid boiled carefully over a free flame, keeping the casserole moving all the time, till copious white fumes are given off (Note 3). The dry or pasty mass remaining is cooled and 125 cc. of water (measured in a graduate) added and the mixture heated till the sulphates of copper and zinc are dissolved. Any lead present will remain as insoluble lead sulphate. It may be filtered on paper, washed with dilute sulphuric acid, one part acid to twenty of water, and finally two or three times with strong alcohol to remove the acid, which would otherwise cause the filter to char during the subsequent drying. The alcoholic washings may be rejected if they are clear. The filter and contents are ignited in porcelain according to 61. During the ignition of the paper a small amount of lead will invariably be reduced, forming tiny metallic globules. These are changed into sulphate by treatment with a few drops of nitric acid followed by a little sulphuric. The excess of acid is driven off and the total sulphate finally ignited at a low red heat. From the weight of  $\text{PbSO}_4$  obtained the percentage of lead is calculated.

If a Gooch crucible (55) is employed the operation is much simplified since no alcohol need be used in the washing and there is no danger of reduction.

### Determination of Copper.

**Procedure.** The filtrate and washings from the lead sulphate are diluted in a 500 cc. graduated flask and thoroughly mixed. A pipetteful representing from 0.3 to 0.5 g. or sample is then used for the determination of copper and zinc. The details of the precipitation of the copper depend on the form of electrodes used. Two schemes will be described.

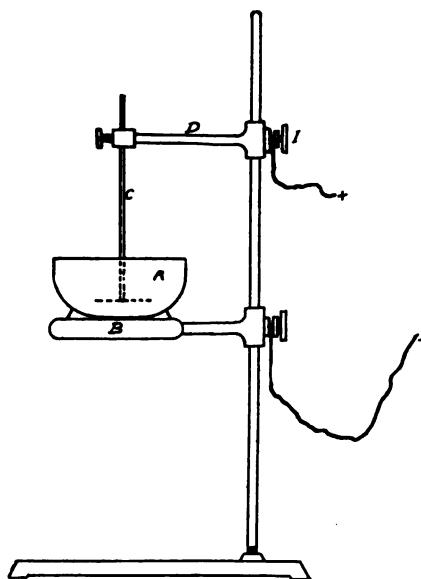


FIG. 8.

(1) The cathode is a platinum dish or crucible. This is set up as shown in figure 8. The support B must be a metal conductor connected with the negative pole of the battery. Contact is made with the outside of the dish merely by setting it on the ring. D is provided with a binding post for attaching the anode C. In the drawing this is represented as a piece of wire coiled at the lower end but any design giving substantially the same extent of surface will serve as well. It is connected with the positive pole. The standard must be of glass or wood to avoid metallic connection between the two electrodes. If a special arrangement of this sort is not at hand, two ordinary ring stands may be used, one

supporting the cathode and one the anode. In any event the whole apparatus should be set up and properly adjusted before a determination is started.

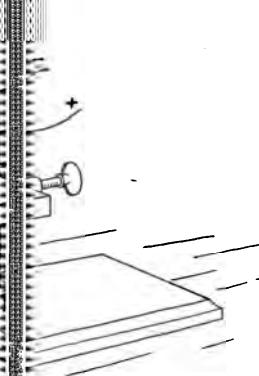
When everything is ready, the dish and anode are thoroughly cleaned (67,3) and the dish heated to redness and placed in a desiccator to cool. It is then weighed and placed on its support and the pipetteful of solution (see above), put into it. About a gram of ammonium nitrate (Note 9) is then added and mixed with the liquid after which the anode is connected and the electrolysis begun (Note 4). The most favorable current density is 0.1 ampere (Note 5). At this rate a bright deposit will be assured, the time required being from 12 to 15 hours, or over night. (See Notes 6 and 7.)

The removal of the dish when the copper is all deposited requires very careful manipulation because the current must not be interrupted while the liquid is acid, for if this were done the copper would immediately begin to dissolve. It is necessary therefore to substitute water for the original contents of the dish which can be done as follows: A small siphon is made as described in 58, filled with distilled water and held so that the liquid will be drawn from the bottom of the dish when it is started. Water is then added from a wash bottle by directing the stream as nearly as possible parallel to the surface of the solution in the dish and at such a rate that the volume of liquid will remain constant. In this manner, by drawing the heavier solution from the bottom and adding water at the top in such a way as to prevent its mixing, the dish will presently be filled with practically pure water. The set screw I is then loosened, the support D carrying the anode raised several inches, and the dish at once removed, emptied into the beaker containing the original solution and rinsed with a little more water which should also be added to the beaker. Beginners should practice this series of operations using water alone before a quantitative determination is attempted.

The dish is finally rinsed two or three times with strong alcohol, dried for several minutes at about 100°, or by holding it over a hot plate or steam box, cooled in a desiccator and weighed. From the weight of copper obtained and the portion of the original sample electrolyzed, the percentage of copper is calculated. (See Note 8.)

## *Chemical Analysis.*

atinum foil dipping into the as shown in figure 9. The ather than low and flat and in the pipetteful of solution ust come above the top edge rk streak would form on the his, water must usually be rge the dilution will not be and anode should be in the



bottom of the beaker. The solution is heated and weighed (Note 3). The solution to-nitrate is then put into the apparatus shown in figure 9 and water added. The distillation may be started (Note 4). The temperature will be the same as given in Note 4. (See Notes 5, 6, 7 and 9.)

be employed as described above. Another plan involving the use of less water is as follows: The support carrying the electrodes is raised so as to expose about one-fourth of the cathode which is then rinsed down with a fine stream from the wash bottle using a specially made nozzle with a small orifice. The next portion of about one-fourth is then exposed and rinsed in the same way and so on till the electrode is raised clear of the liquid in the beaker, care being taken that the next to the last elevation shall leave the lower eighth of an inch or so of both cathode and anode in the solution. The cathode is finally disconnected and dipped once or twice into a small beaker full of alcohol after which it is dried, cooled and weighed as described above for the platinum dish.

#### Determination of Zinc.

**Procedure.** The solution remaining after the removal of the copper, together with the water used in siphoning and rinsing the electrode, is placed in a porcelain dish or Jena glass beaker and brought to a slightly acid reaction by adding first a small amount of ammonia in excess and then dilute nitric acid (1:5) till a piece of litmus paper in the liquid just turns red (Note 11). The mixture is now heated short of boiling and a solution of di-ammonium hydrogen phosphate (Note 12) added in a slow stream from a pipette, using 12 to 15 times the amount necessary to react with the zinc present. The heating is continued—the temperature will be high enough on the water bath or steam box—and the liquid stirred constantly till the precipitate becomes crystalline and settles readily to the bottom. The beaker is then set aside for 3 to 4 hours when the precipitate is filtered into a Gooch crucible (55)—porcelain or platinum—and washed with a hot, one per cent. solution of di-ammonium phosphate (Note 12) till free from sulphates. Several washings are then given with dilute alcohol (1:1) to remove the excess of phosphate. The  $ZnNH_4PO_4$  so obtained may be dried at 100 to 105° and weighed as such or may be ignited as  $Zn_2P_2O_7$ . If the latter procedure is followed, the crucible is placed in a larger one as described in 62, Fig. 4, which is then heated slowly to avoid loss during the driving out of the water and ammonia. The heat is finally increased till the outer crucible is bright red and thus continued till constant weight is reached. (See also Note 13.) The percentage of zinc is finally calculated.

**Notes.** 1. In case antimony is present it will be found in the residue obtained by the evaporation of the nitric acid solution. If, in the course of commercial work this residue is large, it should be investigated further as it is likely not to be pure metastannic acid.

2. The evaporation of the nitric acid solution before introducing the sulphuric acid is merely a trick of manipulation to avoid the violent bumping that would otherwise occur.

3. Beginners are often unable to distinguish the white fumes of sulphuric acid from water vapor. The acid fumes are denser and appear under the cover glass, as well as escaping from the lip of the casserole. They also produce violent coughing if breathed.

4. The dishes or beakers containing a solution undergoing electrolysis should be covered to prevent loss through spray carried out by the gas given off at the anode. The ideal arrangement is a perforated watch glass or a watch glass cut into two pieces with the edges notched to engage the wire supports of the electrodes. Such covers are, however, very fragile and small pieces of plane glass serve almost as well. The notches are easily made with a file.

5. If a large battery or other source of current and the necessary variable resistances and measuring instruments are not at hand, the following practical points may help solve the difficulty: The proper rate of deposition under the conditions of the procedure above will be obtained, approximately at least, with three or four gravity or crow-foot cells in series or one storage battery cell. In case a direct-current 110 volt lighting circuit is in use, it may be employed by taking the current that passes through a 16-candle power incandescent lamp. So far as the precipitation of copper as given above is concerned, one needs only to note the appearance of the deposit. As long as it is bright and adherent, the current may be assumed correct. If darkening shows, the current should be cut down by interposing resistance which can sometimes be done merely by increasing the distance apart of the electrodes. One of the easiest arranged resistances is another electrolytic cell which may be made by two pieces of platinum dipping into a beakerful of dilute acid. It can be varied by changing the distances apart of the electrodes or the concentration of the acid.

6. Completeness of precipitation may be tested as follows:

About 5 cc. are taken out with a pipette, placed in a test tube and an *excess* of ammonia added. If copper is still present a blue color will be produced. If this is the case, nitric acid should be added till the blue disappears and the mixture returned to the main solution. In any event the portion removed must be saved on account of the zinc it contains. If a dish is employed as cathode, water may be added to raise the level of the liquid. It can then be noted whether copper is deposited on the fresh platinum surface.

7. A brown deposit on the anode consists of lead peroxide,  $\text{PbO}_2$ . If it is more than a mere stain, the anode should be rinsed off with water, dried by holding it an inch or so above the hot plate and weighed. The deposit is then dissolved off in nitric acid containing oxalic acid and the electrode again weighed. In this way the amount of lead is determined and may be added to the main portion separated as sulphate.

8. The deposited copper is removed from the platinum by means of dilute nitric acid.

9. Dark colored and non-adherent deposits are as a rule due to too strong current. Certain substances in the solution may, however, be the cause. In such a case it is worth while to try the experiment of shutting off or reversing the current till the copper is redissolved and then connecting again and make the precipitation the second time. This often produces a bright deposit. Some substances also favor a good deposit as for example the ammonium nitrate called for above. In the case of the platinum foil electrodes dipping into the solution the copper oftentimes deposits in a loose feathery form at the edges where the current density is strongest. This must be watched carefully to avoid loss.

10. Trouble is sometimes experienced in placing the platinum foil electrodes in a small desiccator on account of their length. In such an event a suitable desiccator is easily improvised from a wide mouth bottle. As a rule it is not advisable to stand the electrode on its lower edge on account of the tendency of the deposit to be loose at that point.

11. Care must be exercised in order to make the reaction of the solution just barely acid. Zinc ammonium phosphate is soluble both in acid and ammoniacal liquids.

12. About a 1-in-10 (See Note 3 page 137) solution of the di-

ammonium hydrogen phosphate should be prepared by dissolving the salt in water. To insure its proper reaction, a little phenolphthalein (111,3) should be added and then dilute ammonia drop by drop with intermediate stirring or shaking till a pink color is produced. This solution should be filtered or the clear supernatant liquid pipetted, if any insoluble residue exists. The wash water must be prepared from this "neutralized" phosphate solution.

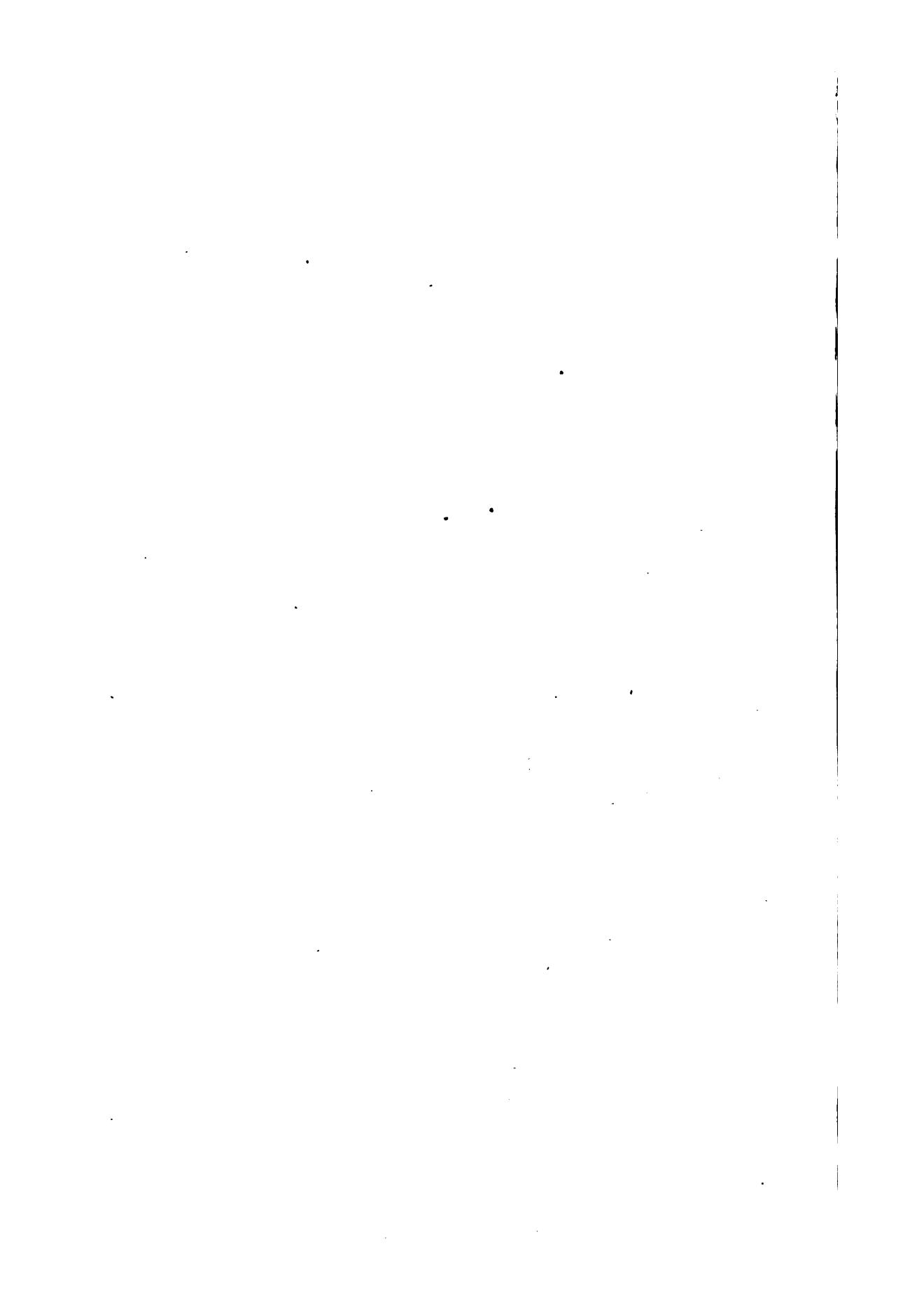
13. Some specimens of asbestos are said to lose weight when washed with ammonium phosphate solution<sup>1</sup>. This point should therefore be tested in the case of at least one of the precipitates. The crucible after weighing is placed in its support on the suction flask and dilute nitric acid poured through till the zinc phosphate is completely dissolved. The asbestos felt is then washed several times with alcohol and the crucible dried or ignited — according to the previous treatment of the precipitate — and reweighed. Appropriate corrections are made for any loss in weight observed.

<sup>1</sup>Dakin. Z. anal. Chemie, 39, 273.

## APPENDIX.

### INTERNATIONAL ATOMIC WEIGHTS, 1910<sup>1</sup>.

	SYMBOL	ATOMIC WEIGHT		SYMBOL	ATOMIC WEIGHT
Aluminium	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.9	Neon	Ne	20.0
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Nitrogen	N	14.01
Bismuth	Bi	208.0	Osmium	Os	190.9
Boron	B	11.0	Oxygen	O	16.00
Bromine	Br	79.92	Palladium	Pd	106.7
Cadmium	Cd	112.40	Phosphorus	P	31.0
Cesium	Cs	132.81	Platinum	Pt	195.0
Calcium	Ca	40.09	Potassium	K	39.10
Carbon	C	12.00	Praseodymium	Pr	140.6
Cerium	Ce	140.25	Radium	Ra	226.4
Chlorine	Cl	35.46	Rhodium	Rh	102.9
Chromium	Cr	52.0	Rubidium	Rb	85.45
Cobalt	Co	58.97	Ruthenium	Ru	101.7
Columbium	Cb	93.5	Samarium	Sa	150.4
Copper	Cu	63.57	Scandium	Sc	44.1
Dysprosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	167.4	Silicon	Si	28.3
Europium	Eu	152.0	Silver	Ag	107.88
Fluorine	F	19.0	Sodium	Na	23.00
Gadolinium	Gd	157.3	Strontium	Sr	87.62
Gallium	Ga	69.9	Sulphur	S	32.07
Germanium	Ge	72.5	Tantalum	Ta	181.0
Glucinum	Gl	9.1	Tellurium	Te	127.5
Gold	Au	197.2	Terbium	Tb	159.2
Helium	He	4.0	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.42
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	119.0
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.85	Tungsten	W	184.0
Krypton	Kr	83.0	Uranium	U	238.5
Lanthanum	La	139.0	Vanadium	V	51.2
Lead	Pb	207.10	Xenon	Xe	130.7
Lithium	Li	7.00	Ytterbium		
Lutecium	Lu	174.0	(Neoytterbium)	Yb	172.0
Magnesium	Mg	24.32	Yttrium	Yt	89.0
Manganese	Mn	54.93	Zinc	Zn	65.37
Mercury	Hg	200.0	Zirconium	Zr	90.6



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